On the possibility of technosphere safety by superionic

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Abstract. The purpose of this article is an attempt to substantiate the possibility of using a new technology for cleaning the industrial atmosphere in a separate workshop of the Taldykorgan battery plant "Kainar AKB", which produces, in particular, powerful batteries for K–700 tractors for agriculture. The innovative technology of air purification proposed by us in the technosphere of the manufacture of batteries for the agricultural production complex is based on the use of transport ion-conducting properties of solid electrolytes made of stabilized zirconium dioxide. The traditional methods of industrial atmosphere purification in enterprises and factories known to us, in our opinion, are morally outdated in terms of bulky external dimensions, noise generation, and need for systematic maintenance. The installation developed by us from a superionic conductor is devoid of these disadvantages, it is low-inertia, does not create a noise effect, compact and small-sized. Our ion conducting solid electrolyte is a ceramic material in the form of pipes, test tubes, tablets, initially containing impurity cations of lower valence, such as calcium, yttrium, scandium, in comparison with zirconium. Actually, these impurity cations create the presence of vacancies or holes in the solid cubic structure of zirconium dioxide. Only oxygen anions will be transported through these vacancies under the effect of external factors, high temperature, and DC electric field. The research method is based on the measurement of the electromotive force, which is recorded at the boundary section: air/superionic/air, which is uniquely mathematically related to oxygen concentration in air stream.

1. Introduction
Modern production of batteries, necessary for many areas of human needs, are equipped with powerful installations for atmospheric air purification in the production facility [1]. In the production of chemical cells, there are technological processes with the release of harmful gas impurities containing lead dust with a significant amount of toxicants in the atmosphere of working facilities. Analysis of the production atmosphere on our example of the Taldykorgan battery plant "Kainar AKB", the concentration of lead dust in the atmosphere of individual plant workshops, where the number of workers about 15 people, was about 40 mcg/m$^3$ (in 17 samples out of 35), and in 8 samples it reached 400 mcg/m$^3$ [4].

In accordance with the basic technological principles of environmentally friendly production, as well as after studying several experimental series of successful implementation of clean production in many sectors of battery production, we have developed a theoretical method for atmospheric air purification in separate workshops of the Kainar battery plant in the city of Taldykorgan, Almaty region for the production of lead batteries. Such a need for the application of our proposed new
technology for plant production atmosphere purification, to obtain environmentally friendly oxygen, is based on the ion transport ability of solid electrolytes from stabilized zirconium dioxide ZrO\(_2\), with an admixture of cations of lower valence, such as Ca\(^{2+}\), Sc\(^{3+}\), Y\(^{3+}\), than that of Zr\(^{4+}\). The phenomenological property of TSCP is exclusively oxygen-ion conductivity under certain external conditions [7].

Until now, the traditional methods of purification of industrial atmosphere of enterprises and factories known to us, in our opinion, are morally outdated in terms of bulky external dimensions, noise generation, need for systematic maintenance and constant care [2]. The technological installation developed by us from a superionic conductor does not have these disadvantages, in operating mode it is quickly included in the measurement of the desired value, low-inertia, does not create a noise effect, compact, small-sized, and light-weight device.

In the next section of our article, we tried, first, to elaborate in detail once again on the objective reasons for the need to purify the atmospheric air of the workshop production facility containing harmful impurities such as lead dust and other impurities harmful for human body. They indicated the main regulatory legal acts, the laws of the Republic of Kazakhstan on which we relied during the writing of this article, such as the Environmental Code of the Republic of Kazakhstan (Code of the Republic of Kazakhstan dated 02.01.2021, No. 400-VI ZRK) [10].

We have revealed the functionality of our technological installation based on an oxygen pump made of a superionic conductor based on stabilized zirconium dioxide. The multimodule laboratory technological installation developed by us, consisting of ceramic superion tubes connected in parallel with each other (tube length of the l order = 160-200 mm, diameter d = 20-50 mm, with a thickness of \( \delta = 2-3 \text{mm} \)), allows to obtain high-purity oxygen with a capacity of 5-8 liters/hour.

2. Materials and Methods

Critical concentrations of lead dust in the working atmosphere of workshops sometimes exceed sanitary standards (Table 1) in terms of the composition of this substance and production waste (Table 2).

| Manipulations                          | mcg/m3          |
|----------------------------------------|-----------------|
| Compound of oxides                     | 250-21600       |
| Preparation of battery plates          | 50-620          |
| Applying lead paste manually           | 150-2700        |
| Applying paste by mechanisms           | 80-13500        |
| Molding                                | 30-2200         |
| Packaging and form removal             | 110-4500        |
| Workshops for plastics                 | 9-12            |
| Lead LOC in plant atmosphere (Russia)  | 10              |
| Natural background analysis            | 0.006-0.012     |
| In the waste of French plants          | 5 (at the rate of 2) |
Table 2. Waste from lead battery plants, USA [6]

| Sources of emissions                          | Permissible emission |
|-----------------------------------------------|----------------------|
| Removing the battery plates                   | 6.3 mg/m³            |
| Paste compound                                | 1.65 mg/m³           |
| Multi-stage technological operations          | 1.65 mg/m³           |
| Making red lead oxide                         | 4.5 mg/m³            |
| Lead deoxidation                              | 74 mg/m³             |
| Lead emissions into the air                   | 16.5 mg/m³           |

As it can be seen, in the production of chemical cells from lead, plates containing many lead compounds are mainly prepared, such as lead dioxide used in the form of paste, which is smeared into a series of grids cast from lead - antimonic alloy (pasteurized plates). The preparation of plates is a complex process that requires contact with molten metal, the danger of which is associated with the spill of oxides that form on the floor a layer harmful to the human body. Mixing of lead oxide paste is accompanied in parallel with the molding of lead grids.

At this moment, as in many technological operations, the main harm is caused by dust of lead oxides, often when loading mixers with powdered compounds. In subsequent operations, pastes are smeared into the plates either manually or with the help of machines. In both cases, toxic dust harmful to the worker body is formed, which accumulates as the paste dries. The final operation is to expose the battery plates to heat treatment and drying in high-temperature furnaces and move them for molding.

In our Republic of Kazakhstan, industrial environmental control is carried out to obtain reliable information about the impact of the nature user on the environment, to assess the effectiveness of environmental protection measures carried out by the nature user, to assess and forecast the consequences of environmental impact.

The assessment of the environment ecological state is achieved by comparing periodically obtained data of controlled parameters with normative indicators. The control objects are atmospheric air, surface and groundwater, soil cover, production and consumption waste generation, background radiation level [3].

Legislative and regulatory acts, requirements for industrial environmental monitoring are largely justified by Articles 129, 131, 132 of the Environmental Code of the Republic of Kazakhstan (Code of the Republic of Kazakhstan dated 02.01.2021, No. 400-VI ZRK) and are fulfilled by all nature users. The monitoring results are drawn up according to the Order of the Minister of Environmental Protection of the Republic of Kazakhstan dated February 14, 2013 No. 16-Ө "Reporting requirements for the results of industrial environmental control". To this date, in the Republic of Kazakhstan, the total number of production monitoring posts installed on the territory of production facilities and enterprises is 190, in which harmful gas impurities for the human body are detected by components online.

Many physical experiments aimed at obtaining environmentally friendly oxygen from the gas flow of the working atmosphere of production and enterprises, as well as from the oxygen-containing gas under study, or, as in our case, from the flow of atmospheric air polluted with lead dust in the workshop, are interested in the development of oxygen dosing methods. To achieve this goal, materials based on oxides of stabilized zirconium dioxide are relevant, characterized exclusively by oxygen-ion transfer in a wide range of temperatures T, and partial pressures of oxygen P1 [9].

In essence, it is a ceramic refractory material ZrO2 +12 mol. % CaO, is a compound cast in the form of pipes, tubes, or tablets, which at T = 1000°C has a specific electrical conductivity σ= 5.5 ×10⁻²
(Ohm ×cm)$^1$ and retains oxygen-ion conductivity almost to the partial pressure of oxygen $P^1 = 10^{20}$ atm. At low oxygen pressures $P$, compared to $P^1 = 10^{20}$ atm, part of the oxygen escapes from the main grid and at this moment the electronic conductivity component, which is not desirable for us, appears at which the superionics material degrades or "recovers". In our case, this is an undesirable side of the superionic conductor operation.

If we separate spatial volumes with different atmospheric pressures $P' > P_x$ from such a superionic ceramic material, then an electromotive force (EMF) $E$ will arise at the air/electrode/superionic interface:

$$E = \frac{RT}{4F} \ln \frac{P'}{P_x}$$

where $R$ is the universal gas constant, $F$ is the Faraday constant, $T$ is the ambient temperature, $P^1$ is the partial oxygen pressure in the surrounding atmosphere equal to $0.21 \times 10^5$ Pa, $P_x$ – the desired oxygen pressure) [8].

3. Results

Our proposed technology for industrial lead dust removal, to regenerate environmentally friendly oxygen, is based on the use of the so-called oxygen pump (OP) – a device for dosing or regulating the oxygen concentration in the gas stream in the workshop (Figure 1).

![Figure 1. Oxygen pump from a superionic conductor. Agreed by the authors.](image)

If we pass a current $I$ from an external source $E$ through such an air/electrode/superionic interface, then we have the ability to control and regulate the oxygen concentration $P_x$ in the flow at a speed $\vartheta$, the atmospheric air under study $P^1$, in the workshop or in a separate plant facility. This is the oxygen pump principle. Thus, in our case of oxygen dosing in a gas stream, the wall of the tube serves as a partition, which forms a pumping PS with one pair of electrodes, and a measuring section (PS and MS) with the other pair.

In case when we pass a production atmospheric gas through the superionic tube at a speed $\vartheta$ containing oxygen in its composition with an initial oxygen concentration $P^1 = 0.21 \times 10^5$ Pa, (here we consider the partial pressure of oxygen in the environment, i.e., its known content in the atmosphere is 21% !) the value of the unknown oxygen concentration $P_x$ at the outlet of the oxygen pump (OP) will
uniquely depend on the magnitude of the current $I$ in the circuit of the pumping section PS of the oxygen pump:

$$I = \frac{RT}{r AF} \ln \frac{P'}{P_x}$$  \hspace{1cm} (2)$$

where $r$ is the resistance of the oxygen pump tube partition or wall. Here, ultimately, we can determine the desired oxygen concentration $P_x$ by the value $E$ measured on the measuring section MS electrodes:

$$P_x = P^1 \cdot \exp \left( \frac{-4FE}{RT} \right)$$  \hspace{1cm} (3)$$

(here $P^1$ is the oxygen concentration or partial pressure outside the tube equal to $0.21 \times 10^5$ Pa).

The main causes of the electromotive force $E$, on the oxygen pump partition, more precisely at the interface of the passing oxygen-containing gas/ electrode material/ ambient air flow, are the following current-forming electrode reactions:

- on the cathode $O_2 + 2e = O_2^{-}$, \hspace{1cm} (4)
- on the anode $O_2^{-} - 2e = O_2$↑ \hspace{1cm} (5)

The multimodule laboratory installation developed by us, consisting of ceramic superion tubes connected in parallel with each other (tube length of the l order = 160-200 mm, diameter $d = 20-50$ mm, with a thickness $h = 2-3$ mm), allows to obtain high-purity oxygen with a capacity of 5-8 liters/hour (Figure 2), compiled by the authors.

![Multimodule installation of superion tubes](image)

**Figure 2.** Multimodule installation of superionics tubes. Compiled by the authors.

In the course of the experiment, we can calculate elementary variables, such as the volume and mass of the resulting environmentally friendly oxygen, at first theoretically calculating the workshop area and volume in standard form:

$$S = a \cdot b, \hspace{1cm} [m^2]$$  \hspace{1cm} (6)$$

here $a$ is the workshop length [m], and $b$ is the workshop width [m].

$$S = a \cdot b = 5 \cdot 4 = 20, \hspace{1cm} [m^2]$$  \hspace{1cm} (7)$$
\[ V = S \cdot h, \text{[m}^3] \] \tag{8}

Here \( S \) is the workshop area [m\(^2\)], where \( h \) is the workshop height [m].

\[ V = S \cdot h = 20 \cdot 4 = 100, \text{[m}^3] \] \tag{9}

We will assume that the air inside the workshop is under normal conditions, i.e. \( T \) is the temperature of 273 K, and the total atmospheric air pressure is \( P = 1 \text{ atm.}, \) i.e. \( P = 10^5 \text{ Pa}. \) The oxygen molar mass \( \mu_{\text{O}_2} = 29 \cdot 10^{-23} \text{ kg/mol}, \) \( R = 8.31 \text{ kg/mol [J / (mol•K)]}, \) \( m \) is the mass of oxygen in the chamber [kg].

Solution:

We will use the Mendeleev-Klayperon equation describing the state of any gases:

\[ PV = mRT / \mu \] \tag{10}

From here we find the air mass in the workshop we need,

\[ m = \mu PV / R \] \tag{11}

\[ m = 29 \cdot 10^{-3} \cdot 105 \cdot 102 / 8.31 \cdot 273 = 29 \cdot 104 / 24 \cdot 102 = 1.2 \cdot 102 = 120 \text{ kg}, \] \tag{12}

Considering that the oxygen content known to us in the total air is 21%, then the mass of all oxygen found by us is \( m_{\text{O}_2} = 93.6 \text{ kg}! \)

If we divide the number \( V = 100 \text{ m}^3 \) by the volume of machines or devices in the workshop found above, we will find the air density \( m_{\text{O}_2} = 93.6 / 100 = 0.936 \text{ kg/m}^3. \) This value, definitely, is very small per person! We considered this report in an ideal form, but in fact, in the workshop, according to sanitary norms and rules (SNiP), fans work in due time and maintain necessary standards! In addition, we can also determine the experimental value of the number of oxygen molecules \( N \), in the mass \( m \) found above. To do this, we will again resort to the formula (10), from which it follows that the mole of the released oxygen is equal to:

\[ \hat{\mu} = m / \mu = PV / RT \] \tag{13}

Then, considering the dependence \( m / \mu = N / N_A \), we find the desired value, the number of oxygen molecules

\[ N = N_A \cdot m / \mu = 6 \cdot 10^{23} \cdot 120 / 29 \cdot 10^{-23} = 24 \cdot 10^{26} \text{ oxygen molecules}. \] \tag{14}

4. Discussion

It is safe to say that the possibility of using an oxygen pump (OP) made of a solid ceramic electrolyte consisting of stabilized zirconium dioxide for the dosage and regulation of oxygen concentrations in the atmospheric air gas stream of production can be justified on the basis of the following factors:

- presence of exclusively oxygen-ion conductivity in TSCP under the effect of external, regulated quantities, such as high temperature, DC electric field;
- all phenomena and processes on the solid electrolyte under study are divided into the mass transfer of oxygen from the flow to the surface of the electrodes and the production of environmentally friendly oxygen;
- physical adsorption of oxygen molecules on solid electrolyte electrodes;
- regulated by mass transfer through a porous electrode to the electrode – superionic interface, followed by ionization of oxygen atoms into a stream of molecular oxygen regulated by DC from an external source;
- entry of oxygen molecules from a passing stream of oxygen-containing gas, by adsorption and addition of electrons at the cathode, according to the electrode reaction (4);
- transfer of oxygen anions to the outside via superionic (they are released as pure molecular oxygen at the anode, according to the electrode reaction) (5). Obtained theoretical results and calculations based on empirical equations (1), (2), (3) are consistent with the expected practical data.
We indisputably agree that the method we have developed for atmospheric air purification at the production facility from harmful lead dust and other harmful gas mixtures is low–power in terms of the productivity of obtaining environmentally friendly oxygen - compared with existing production plants for atmospheric air purification at the production () and with known dust level measuring methods [11]. But at the same time, we are confident in the advantage of the novelty and suitability of the technological installation - the oxygen pump based on solid electrolyte for obtaining environmentally friendly oxygen at the production:
- it is low-inertia, small-sized, and noiseless, compared with dimensional aspiration installations, bag filters, and Cyclone filters, scrubbers, etc.;
- deep pumping of oxygen concentration from the gas medium up to \( P_x = 10^{-21} \) atm.;
- specific selectivity in the determination and regulation of oxygen concentration in any gas environment.

5. Conclusions
Based on the above and the results obtained, we were able:
- to substantiate the theoretical and practical significance of using environmentally friendly oxygen concentration dispenser made of solid electrolyte based on stabilized zirconium dioxide under certain external, possible conditions;
- to apply physical equations to obtain the experimental values of the quantities we are looking for, such as the oxygen concentration \( P_x \), expressed in units of partial pressure, the total mass of oxygen per unit volume of the facility, the number of oxygen molecules in workshop;
- and finally, the possibility to obtain environmentally friendly oxygen by pumping it out of the total atmospheric flow of production gases using a process plant based on TSCP.

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