Derivation of the equation of state for a superionic conductor

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Abstract. The purpose of this article is an analytical consideration of the features of the physical characteristics of the quantities of a high-temperature ceramic solid oxide superionic conductor, using the example of an oxygen pump made of stabilized zirconia. Based on the consideration of an elementary axial section of a superionic tube with geometric data on the length, thickness, and diameter of the tube, an equation was obtained that relates all adjustable quantities of an oxygen pump in the entire range of oxygen dosing, in particular, to select the geometric dimensions of the device and the optimal ratios of controlled quantities. The derivation of such an equation for the pumping section of an oxygen pump is based on a number of assumptions as for an idealized oxygen pump. The current-voltage characteristic of an oxygen pump in the region of deep pumping, associated with the appearance of electronic conductivity of the ceramics of the pumping section of the oxygen pump, leading to its destruction, electrochemical aging or degradation, has been studied. It is substantiated that the volt-ampere characteristic of the oxygen pump is the only informative curve, which is used to judge the correct mode of operation of the superionic pump and prevent the onset of electrochemical degradation. When developing a research method and setting problems for a ceramic oxide superionic conductor, a number of assumptions were taken into account, as for an idealized electrolyte. The considered solid oxide superionic conductor or solid electrolyte is a ceramic material in the form of tubes, test tubes, tablets, initially containing impurity cations of lower valence, such as calcium, yttrium, scandium, than zirconium. It is these impurity cations that create the presence of vacancies or holes in the solid cubic structure of zirconium dioxide. Through these vacancies, under the influence of external factors, high temperature and direct current electric field, only oxygen anions will be transported. The research method is based on the measurement of the electromotive force, which is recorded at the boundary section: air/electrode/superionic, unambiguously related mathematically to the oxygen concentration in the air flow. Mathematical formulas are given for calculating the desired oxygen concentration depending on various external conditions. Theoretical conclusions and substantiations on the possibility of using the phenomenological transport properties of a superionic conductor under production conditions are presented.

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1 Introduction

Many processes in the technosphere around us, in production and industry in the manufacture and receipt of all products for mankind, occur in contact with an oxygen-containing atmosphere. The protection and protection of the environment, the life of the entire living and plant world, the biosphere are due to the presence of oxygen in the atmosphere, its share is known to be 21% in it, or in terms of its partial pressure in the general atmosphere \( P_1 = 0.21 \cdot 10^5 \text{ Pa} \) [1].

In addition, the current pace of development of innovative technologies in the field of science and technology, the production of nanomaterials, cleaning the industrial atmosphere in the room from dust and harmful gases, setting up physical experiments, and synthesizing new materials are interested in the development of oxygen dosing methods. In this sense, many problems of dosing or controlling oxygen concentrations can be solved using the transport properties of ceramic solid oxide superionic conductors (SOSC). These are impurity ionic conductors, called high-temperature or oxide solid electrolytes, as in our case, based on stabilized zirconia.

Chemical and thermophysical properties, as well as polymorphic transformations and stabilization of zirconia (ZrO_2) are well described in the literature, for example [4, 7]. Pure zirconia is a ceramic material that melts at a temperature \( T = 2070^\circ\text{C} \), has a low, temperature-independent thermal conductivity, and high chemical resistance. But these advantages are difficult to use, since below \( (2000^\circ\text{C}) \) there are two modifications - monoclinic and tetragonal [2].

Reversible between them, slowly flowing at a temperature below \( (1200^\circ\text{C}) \), is accompanied by volumetric compression by 7.7%. The third modification, cubic with a fluorite structure, is stable in pure oxide only at very high temperatures. However, the ceramic used, as in our case, can be stabilized in the form of a cubic modification over the entire temperature range by adding divalent or trivalent cations with a radius close to the ionic radius \( (\text{Zr}^{4+}) \).

Stabilization patterns and transport properties of cubic zirconia are shown in the sources [3]. Many oxides, such as (CaO, Sc_2O_3, Y_2O_3), and rare earths form substitutional solid solutions with zirconium dioxide with a wide temperature range. And most importantly for us, the lack of charge of impurity cations is compensated by anion vacancies, the concentration of which is thus set by the concentration of impurity cations. These anionic vacancies carry out the transfer of oxygen anions (O^{2-}). Therefore, stabilized zirconia (ZrO_2), along with excellent refractory properties, exhibits ionic electrical conductivity, which does not depend on the partial pressure of oxygen in the surrounding gas \( (P_{O_2}) \) and increases exponentially with temperature \( T \) due to an increase in carrier mobility. Table 1 provides details of the stabilized zirconia of the most commonly used formulations.

<table>
<thead>
<tr>
<th>Table 1. Properties of stabilized zirconium dioxide at ( T=1000^\circ\text{C} ).</th>
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<tr>
<td><strong>Stabilizing additive</strong></td>
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<td>Region of existence of solid solutions with a fluorite structure (additive concentration, mol.%)</td>
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<td>Concentration of anion vacancies, in %</td>
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In the reviewed literature sources on the study of ceramic superionic oxygen conductors, [4, 6] the increased interest in oxygen dosing in melts and in a gaseous atmosphere prevails over solid samples, and it is also clear that the engineering trend is
ahead of research into the oxygen dosing process itself.” In general, the literature review concludes that there is no research phenomenological theory of the oxygen pump [7-9].

In the next section of the article, an attempt is made to derive an analytical consideration of the main aspects of the oxygen pump, to obtain and investigate the equation for the current-voltage characteristic of the pumping section of the oxygen pump to select the geometric dimensions of the device and the optimal ratios of the controlled values, as \((P^1, P_o, T, U, \theta)\), where \(P^1\) is the partial pressure of oxygen in the general atmosphere, \(P_o\) is the initial pressure of oxygen in the gas flow, \(T\) is the ambient temperature, \(U\) is the voltage applied to the electrodes, \(\theta\) is the gas flow rate.

### 2 Materials and methods

The purpose of the study is to find the threshold value of the desired oxygen concentration in any flow of oxygen-containing inert gas in the industrial atmosphere. To achieve this goal it is necessary:

- Derive, solve and investigate the equation of distribution of oxygen concentration along the length of the pumping section of an ideal oxygen pump, depending on the process conditions and device parameters (on \(T\) - temperature, \(I\) - current, \(L, D\) - respectively, on the length and diameter of the ceramic superionic tube).
- Obtain and investigate the equation of current-voltage characteristics of the pumping section of an ideal oxygen pump.
- To investigate the main experimental characteristics of the oxygen pump.

![Fig. 1. Electrochemical or ceramic oxygen pump for dosing oxygen in a neutral gas stream.](image)

This is a tube of solid ceramic electrolyte heated to a temperature \(T\) with inert electrodes (1 internal and 2.3 external), consisting of pumping and measuring sections connected in series. An inert gas or nitrogen with an initial partial pressure of oxygen \(P_o\) is passed through the tube at a speed \(\theta\) (m³/s). The partial pressure of oxygen \(P^1\) is maintained outside the tube. The total pressure \(P\) outside and inside the tube is 1 atm. The partial pressure of oxygen at the outlet of the device \(P\) depends on the regulated current in the circuit of the pumping section. \(P\) is determined from the results of measuring the electromotive forces (EMF) of the measuring section E. Obviously, the geometric dimensions of the pumping section and the electrical conductivity of the solid electrolyte \(\sigma = \sigma(T)\) are parameters of the oxygen pump, \(P^1\) and \(P_o\) describe the set conditions, while \(T, \theta\) and voltage \(U\) represent the controlled values. In essence, an oxygen pump is an energy converter, like a four-terminal network:
For a complete study of the characteristics of an ideal oxygen pump, the following operating conditions are allowed:

- There is no galvanic connection between the pumping and measuring sections.
- Cross flow of oxygen does not change the value $\vartheta$ of the flow rate.
- Transverse mixing of the gas is sufficient, there is no counter longitudinal diffusion of oxygen.
- Electrode reactions proceed quickly:
  - Equilibrium between molecular and ionized oxygen at three-phase boundaries (air/electrode/SOSC) is achieved.
- Solid oxide superionic conductors retain vacuum density and exclusively oxygen ion conductivity over the entire range of $T$ and $P$ under consideration;
- Molecular oxygen in the working gas does not dissociate into atoms.
- The initial gas mixture does not contain oxygen-containing (buffer) gases.

### 3 Results

Obviously, for a given material and geometry of a tube made of solid oxide superionic conductors, as well as for given $P_1$ and $P_o$, each required value of $P$ can be a set of combinations of $T$, $\vartheta$, and $U$. Therefore, to study the capabilities of an oxygen pump over the entire dosing range, in particular, to select the geometric dimensions of the device and the optimal ratio of the controlled values, it is necessary to have an equation linking the listed parameters. The derivation of such an equation for the pumping section of an oxygen pump is derived from considering the elementary axial section of a tube made of solid oxide superionic conductors with an inner diameter $D$ and a wall thickness $h$, in Figure 3.
As shown in Figure 3, the x-axis of the Cartesian coordinate system is aligned with the tube axis, the direction of the x-axis coincides with the direction of the gas flow, and the origin of coordinates lies in the end section. An electric potential difference is maintained between the outer and metallized surfaces of the tube

\[ U = \varphi_1 - \varphi, \]

where \( \varphi_1 \) is the potential of the outer electrode, \( \varphi \) is the potential of the inner electrode. The partial pressure of oxygen inside the tube \( P_x \) depends on the x coordinate. The tube wall in section x is found by the action of the difference in the chemical potentials of oxygen \( \Delta \mu = \mu_1 - \mu_x \), where \( \mu_1 = \mu^0 + RT\ln P^1 \) and \( \mu_x = \mu^0 + RT\ln P_x \) are the chemical potentials of oxygen from the outer and inner surfaces of the tube. The electrical conductivity of the tube material \( \sigma \) is given as a function of temperature. Observing the condition \( h \leq D \) allows us to accept

\[ \frac{\partial \varphi}{\partial y} \leq \frac{U}{h}, \quad \frac{d\mu}{dy} \leq \frac{\Delta \mu}{h}. \]

It is required to compose an equation relating the stationary value of \( P_{o2} \) in an arbitrary section x with the device parameters \( D, h, \sigma(T) \), input data \( P^1, P_o, \vartheta \) and controlled values \( T \) and \( U \). Considering the equation of state of the gas, it is possible to write for the increment in the number of moles of oxygen \( \Delta M_x \) in the volume \((\pi D^2 / 4)\) dx on the way (x-o) to write:

\[ \Delta M_x = (\pi D^2 / 4RT) \cdot (P_x - P_0) \]  

Where \( \Delta M_x \) is the mass of oxygen in the elementary volume of the tube, \( \pi D^2 / 4 \) is the cross-sectional area of the ceramic superionic tube with diameter \( D \), \( R \) is the universal gas constant, \( T \) is the temperature, \( P_x \) is the desired oxygen concentration in section x, \( P_0 \) is the initial initial oxygen concentration. The exclusively anionic conductivity of the tube material, along with the absence of through porosity, allows us to represent the same value as a function of the electric current density through the inner wall of the tube \( j_x \):

\[ \Delta M_x = (\pi D^2 / 4FT) \cdot \int_0^x j_x \vartheta \, dx \]  

Here \( j_x \pi D \, dx \, d\tau \) is the amount of negative electricity transferred through the wall of the tube section dx by oxygen ions coming from the atmosphere into the volume \((\pi D^2 / 4)\) dx in the x section during the time \( d\tau \), \( 4F \) is the amount of electricity that ensures the transfer through the electrolyte of one mole of doubly ionized oxygen. From (1) and (2), taking into account the expression \( \vartheta = (\pi D^2 / 4) \cdot dx / d\tau \), it follows:

\[ P_x = P_0 + \pi D \cdot RT / 4F \vartheta \int_0^x j_x \, dx \]  

In particular, for \( P_{o2} \) at the outlet of a tube of length L, we can write:

\[ P = P_o + RT / 4F \cdot I / \vartheta \]  

Where I is the electric current through the wall. Equation (4) is convenient for practical use, but it does not give an idea either about the nature of the \( P_{o2} \) distribution along the length of the device, or about the dependence of \( P \) on the geometry and properties of the tube material. We represent the current density in the form:

\[ j_x = j_{q_x} + j_{\mu_x} \]
Where \( j_\varphi \) and \( j_\mu \) are the current densities associated with the directed motion of \( O^2^- \) ions in the electric and oxygen concentration fields, respectively. By analogy with conductivity in an electric field, we obtain:

\[
\sigma = j_\varphi \frac{\partial \varphi}{\partial y} = q\cdot n\cdot u_\varphi
\]  

(6)

Let us introduce the concept of diffuse conductivity:

\[
\sigma_\mu = j_\mu \frac{\partial \mu}{\partial y} = q\cdot n\cdot u_\mu
\]  

(7)

Where \( q \) and \( n \) are the charge and concentration of carriers, then \( u_\varphi = \frac{dy}{d\tau} \), \( u_\mu = \frac{d(\varphi, \mu)}{dy} \) are the carrier mobilities in the electric and oxygen concentration fields, respectively. Obviously, \( \sigma_\mu / \sigma = \frac{d\varphi}{d\mu} \), here \( d\varphi \) and \( d\mu \) are increments along the path \( dy \) of the electric energy of \( O^2^- \) ions carrying one pendant and the “chemical” energy of \( O^2^- \) ions constituting one mole, respectively. It follows from the law of conservation of energy that, referred to the same number of particles, these increments of energy have equal absolute values and opposite signs, i.e., \( 4F \, d\varphi = - \, d\mu \). This implies:

\[
\sigma_\mu = - \frac{\sigma}{4F}
\]  

(8)

Taking into account equations (6), (7), and (8) we can rewrite (5) in the form:

\[
j_x = \frac{RT}{4F} \cdot \sigma / h \cdot \ln \frac{P_1}{P_x} - \frac{RT}{4F} \cdot U
\]  

(9)

Substituting (9) and (3) gives us the desired expression for the distribution of \( P_{O_2} \) along the length of the tube:

\[
P_x = P_0 + \frac{(RT)^2}{4F} \cdot \pi D \cdot \sigma / h \cdot \ln \frac{P_1}{P_x} - \frac{RT}{4F} \cdot U \cdot x - \int_0^x \ln P_x \cdot dx
\]  

(10)

The physical meaning of equation (10) is easy to see by rewriting it in the form:

\[
P_x = P_0 - \frac{RT}{4F} \cdot \sigma / h \cdot U \cdot x + \frac{(RT)^2}{4F} \cdot \pi D \cdot \sigma / h \cdot \ln \frac{P_1}{P_x} - \int_0^x \frac{P_1}{P_x} \cdot dx
\]  

(11)

Indeed, the first term on the right side of the equation is the oxygen pressure in any section of the flow in the absence of both electric and oxygen concentration fields, and the second term shows how much \( P_{O_2} \) decreases in an arbitrary section of the flow due to the action of the transverse electric field alone, the third term describes the opposite action of the transverse oxygen concentration gradient. Obviously, each combination of parameters corresponds to a certain maximum achievable value of the partial pressure of oxygen \( P_{pr} \).
Denote, $P_0 = \Pi, (4F/RT) - U - \ln P^V = A, RT/4F)^3 \cdot \pi D \cdot \sigma / h = B$ and rewrite equation (10) in the form:

$$P_x = \Pi - A \cdot B \cdot x - B \cdot \int_0^x \ln P^x \cdot dx$$  \hspace{1cm} (12)

Differentiating (12) with respect to $x$ and substituting $dp/dx = 0$, we obtain for the limiting value:

$$P_{np} = P_1 \cdot \exp (\cdot 4F/RT \cdot U/T)$$  \hspace{1cm} (13)

And in solution (13) with respect to $U$, we get:

$$U = RT/4F \cdot \ln P^V/P_{np}$$  \hspace{1cm} (14)

It is not difficult to find out the well-known formula of an oxygen pump.

A number of works are devoted to the study of the oxygen pump (OP), for example [9-10]. In [10], questions of the phenomenological theory of WH were considered.

The theoretical current-voltage characteristic (CVC) of an idealized device was studied under the assumption that solid oxide superionic conductors retain exclusively oxygen-ion conductivity under all conditions, including arbitrarily low oxygen concentrations in the gas [11].

**Fig. 4.** Volt-ampere characteristic of the oxygen pump.

In the area of deep pumping, it ends with a vertical section $In$ (Figure 4, a) at saturation current

$$I_n = \frac{3}{p - 0} I = p_0 \cdot v \cdot (4F/RT)$$  \hspace{1cm} (15)

When the carriers supplied by the inlet gas flow are completely used up, a further increase in the current through the pumping section (CS) is impossible.

On a real current-voltage characteristic, upon reaching a certain voltage $U_v$-recovery voltage, a further increase in current is observed (Figure 4, b), which is associated with the appearance of electronic conductivity in the CS material due to its recovery at low $p$ [12].

The patterns of VC behavior in this region have not been discussed in the literature. At the same time, it is VC that can serve as a source of information on the course of reduction of
the CL material. It is undesirable to allow the development of reduction, since it slows down the regulation and accelerates the aging of the electrolyte. Here, some features of the VC associated with the reduction of the electrolyte will be considered.

Thus: - when operating a ceramic oxygen superionic conductor, it is necessary to be guided by the course of the current-voltage curve, indicating the beginning of the electrical aging of the superionic at the value of Uv-recovery voltage.

4 Discussion

So, the possibility of using an oxygen pump based on a solid oxide superionic conductor made of stabilized zirconium dioxide for dosing and controlling oxygen concentrations in the gas flow of atmospheric air in production can be justified on the basis of the following factors:

- The presence of an exclusively oxygen-ionic conductivity in a solid oxide superionic conductor under the influence of external, controlled quantities, such as high temperature, a direct current electric field.
- All processes occurring in a solid oxide superionic conductor are divided into the mass transfer of oxygen from the flow to the surface of the electrodes.
- Adsorption of oxygen molecules on the electrodes of a solid oxide superionic conductor.
- Stable mass transfer through the porous electrode to the electrode-superionic interface and ionization of oxygen atoms by a controlled direct current from an external source.
- The entry of oxygen molecules from the passing flow of oxygen-containing gas, by adsorption and the addition of electrons at the cathode.

All tasks were solved in the following way:

- Equations for the distribution of oxygen concentration along the length of the pumping section of an ideal oxygen pump are derived and investigated depending on the process conditions and device parameters (10), (11), (13), (14).
- Obtained and investigated the equation of current-voltage characteristics of the pumping section of an ideal oxygen pump.
- Investigated the main experimental characteristics of the oxygen pump. The author undeniably agrees with the fact that the developed analytical method for regulating the main quantities of the oxygen pump mode does not claim to absolutize its advantages over other methods [10-12].

5 Conclusion

Based on the above and the results obtained, we managed to:

- To substantiate the theoretical significance of using an oxygen pump based on a solid oxide superionic conductor made of stabilized zirconium dioxide under certain external, possible conditions.
- 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 passing air flow.
- And finally, the possibility of obtaining complete information about the operation of the oxygen pump using a current-voltage characteristic that prevents degradation from occurring.

The practical significance of using the proposed ceramic oxygen pump lies in the advantage of dosing and regulating the oxygen concentration to a deep threshold value, of
the order of $P_x = 10^{20-22}$ atm., in any oxygen-containing inert gas of the industrial technosphere.

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