Study of Electrical Conductivity Superionic Conductor

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Abstract: The possibility of analytical determination of the type of electric current conductivity by a solid oxide ion conductor based on stabilized zirconium dioxide (solid electrolyte, superionic) under the influence of a DC electric field and high temperature in the range of 500°-900° degrees is considered. The research objectives of this work are to mathematically interpret the phenomenal phenomenon of substance transfer and irreversible changes in a solid oxide electrolyte (or superionics) of an oxygen concentration cell with mixed electrolyte conductivity. The connection with the need to expand the temperature range of the method and the range of ceramic materials under study is shown. It is confirmed that the sample has a mixed conductivity due to O^{2-} anions, Me+ cations and electrons with non-zero concentrations of $n_{a,k,e}$, charges $q_{a,k,e}$ and mobility in the field of electric forces. A mathematical formula for determining the mobility of anions and cations in a solid oxide superionic conductor based on stabilized zirconium dioxide is derived.

Keywords: Current, Solid, Electrolyte, Oxide, Ionic, Superionic

1. Introduction

To study the type of conductivity of oxide ceramic materials based on stabilized zirconium oxide, the method of oxygen concentration electromotive force (EMF) is becoming increasingly widespread. The analytical consideration undertaken in our work of the transfer of matter and irreversible changes in the solid oxide ion electrolyte (or superionics) of an oxygen concentration cell in the case of mixed electrolyte conductivity is associated with the need to expand the temperature range of the method, as well as to expand the range of ceramic materials under study.

2. Materials and Methods

The transport properties of solid oxide superionic conductors are the basis for various applications. On a partition made of such a material, equipped with inert electrodes and separating media with different chemical oxygen potentials (Figure 1a), there is an oxygen concentration electromotive force (EMF) proportional to the logarithm of the ratio of oxygen concentrations

$$\varepsilon = t_u \cdot \frac{RT}{4F} \cdot \ln \frac{P^1_{O_2}}{P^2_{O_2}} \qquad (1)$$

here R is the universal gas constant, F is the Faraday number. The expression differs from the Nernst formula by the multiplier "ionic fraction of the conductivity of the ionic dialectic" tu. Such cells "without transfer" are used for thermodynamic studies, for gas analysis for oxygen and for measuring the ionic fraction of the conductivity of oxide dialectics [1].

If in such a system an ion dielectric - an electronic conductor - oxygen-containing media electrodes are closed to a passive load, (Figure 1b), then a current will flow in the circuit proportional to the logarithm of the ratio of oxygen concentrations. Such cells "with transfer without an external source" are used as fuel cells.
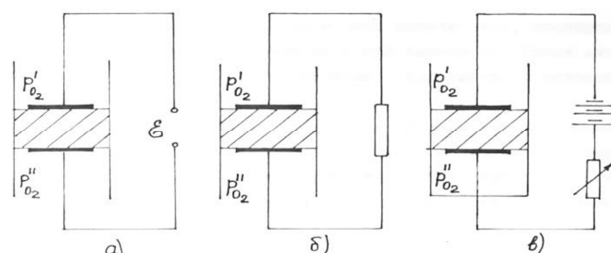

Figure 1. The main types of concentration cells from the TOP.

If a current from an external source is passed through such

a system, it is possible to regulate the oxygen content in one of the volumes (Figure 1). The increment of oxygen concentration in volume V during time τ is proportional to the current integrated during this time,

$$\Delta p = \frac{RT}{4FV} \cdot \int_0^\tau i d\tau \qquad (2)$$

Such a cell "with transfer from an external source" is the most general model of an oxygen pump - an oxygen dosing device using solid oxide ion conductors.

Since the mid-60s, many works have been published, mainly by physicochemists and electrochemists, devoted to the study of known and the search for new solid oxygen-ion conductors, as well as the development of their applications. The last and largest generalization was the monograph by V. N. Chebotin and M. V. Perfiliev [2].

The range of applications of the stabilized ZrO_2 is expanding. By measuring the EMF of electrochemical cells with an electrolyte from stabilized ZrO_2, in addition to thermodynamic measurements and gas analysis, kinetic and diffusion studies are carried out to measure oxygen activity in molten metal, temperature measurement, gas permeability control. Stabilized ZrO_2 is used as a reference in the development of methods for measuring the ionic fraction of the conductivity of oxide ceramic materials [3].

In addition to fuel cells, transfer cells are used in electrolyzers to decompose water and CO_2 to produce oxygen and hydrogen, to separate oxygen isotopes, to study the stoichiometry of oxides, deoxidation of metals, growing VO_2 single crystals from a V_2O_5 melt, as well as for electrochemical molding of vanadium phosphate glasses [4]. One of the promising applications of "transfer cells" is the dosing of oxygen in gases.

3. Results and Discussion

In this regard, materials based on IV B oxides are promising - impurity solid oxide ion conductors (SOIC), also called high-temperature or solid oxide electrolytes. They differ exclusively in oxygen-ion transfer in a wide range of temperatures T, and partial pressures of oxygen P. The high-temperature cubic modification of zirconium dioxide ZrO_2 with a fluorite lattice is stabilized over the entire temperature range by the addition of cations of lower valence. The lack of charge is compensated by active vacancies, through which the transfer of oxygen anions O^{-2} is carried out. Solid solution of ZrO_2 +12 mol. % CaO at T=1000°C has a specific electrical conductivity σ=5,5 · 10^{-2} (Om · cm) $^{-1}$ and retains the ionic fraction of electrical conductivity $t_u \geq 0,99$ up to the partial pressure of oxygen P=10^{-20} atm. At lower pressures P, part of the oxygen leaves the lattice, the charge is compensated by electrons, the electronic component of conductivity increases, the electrolyte material degrades and "recovers" [5].

The material under study acts as a solid electrolyte based on stabilized zirconium oxide. On its electrodes, from the moment of time τ=0, the difference in chemical potentials of oxygen is maintained by μ_1 - μ_2=μ. The stationary EMF of such a concentration cell is proportional to the average electrolyte ionic fraction of conductivity ti

$$\mathcal{E} = t_и \cdot \frac{\Delta\mu}{4F} \qquad (3)$$

regardless of whether it is caused by cations or anions.

Indeed, if the sample has a mixed conductivity due to the O^{2-} anion, Me^+ cations and electrons with non-zero concentrations of $n_{a,k,e}$, charges q $_{a,k,e}$ and mobility in the field of electric forces

$$u_{a,k,e} = \frac{(dx/d\tau)a,k,e}{grad\mu} \qquad (4)$$

then, obviously, under the action of chemical forces grad μ, the anions and cations of this sample will show a mobility other than zero

$$u_{\mu i} = (dx/d\tau)_i) / grad\mu \qquad (5)$$

by analogy with the electrical conductivity of some kind of carriers

$$\sigma_i = j_i / grad \varphi = (q \cdot n \cdot u)_i \qquad (6)$$

we introduce the concept of its "diffusion conductivity"

$$\sigma_{\mu i} = j_{\mu i} / grad\mu = (q \cdot n \cdot u_\mu)i \qquad (7)$$

here (j, jμ) i are the current densities in A/m^2 caused by the movement of the i-th type of particles in the electric and oxygen concentration fields, respectively. Obviously, for electrons it is possible to write $\sigma_{\mu e}$=0, then the ratio of these conductivities for anions and cations has the form

$$\left(\frac{\sigma_\mu}{\sigma}\right)_{a,k} = \frac{\left[qn\left(\frac{dx}{d\tau}\right)\right]a,k \cdot grad\varphi}{grad\mu \cdot \left[q \cdot n \cdot \left(\frac{dx}{d\tau}\right)\right]a,k} = \frac{d\varphi}{d\mu} = -\frac{d(W/Q)}{d(W/M)a}, \qquad (8)$$

where W is energy, Q is the amount of electricity, M is the mass in moles. The "minus" is due to the mismatch of the signs (dx/dτ)/gradμ and (dx/dτ)/gradφ for both anions and cations. Assuming that the charge distribution in the total mass of the anions involved in the conduction is uniform, we proceed to the final increments and write

$$\frac{d(W/Q)}{d(W/M)a} = \frac{W/Q}{(W/M)a} = \frac{1}{(Q/M)a}, \qquad (9)$$

where (Q/M) a is the charge in coulombs carried by one mole of oxygen at the zth degree of its ionization. Further

$$(Q/M)_a = e \cdot z \cdot k \cdot N_a = z \cdot k \cdot F, \qquad (10)$$

where e is the electron charge, k is the number of atoms in the molecule, NA is the Avogadro number, F is the Faraday number. Since for O_2 ions - (Q/M)a = 4F, and expression (3) is equally valid for cations and anions, then we can write
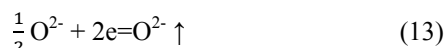
$$\sigma_{\mu a} = -\frac{\sigma_a}{4F}, \sigma_{\mu k} = -\sigma_k/4F. \qquad (11)$$

Let the sample have no macroscopic defects through which molecular oxygen could diffuse. Then the tendency to

spontaneous alignment of $\mu_I > \mu_2$, existing in the system at $\tau \geq 0$, can be realized only through the diffusion of mobile anions and cations. Let's consider their behavior in an oxygen concentration field. Mobile anions O^{2-} form a flow of oxygen in the electrolyte and, accordingly, a negative charge in the direction of μ_2. Oxygen is released at this electrode and a negative charge occurs according to the reaction
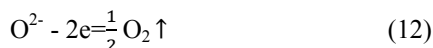
$$O^{2-} - 2e = \tfrac{1}{2} O_2 \uparrow \qquad (12)$$

On the side of μ_1, oxygen enters the electrolyte, and the electrode is charged positively according to the side of μ_1, oxygen enters the electrolyte, and the electrode is charged positively according to the reaction

$$\tfrac{1}{2} O^{2-} + 2e = O^{2-} \uparrow \qquad (13)$$

4. Conclusion

Mobile cations form a flow in the electrolyte towards μ_I [6-8]. The excess cations approaching the electrolyte boundary bind the corresponding amount of oxygen from the medium with its higher concentration, forming new electrolyte layers at this boundary. The electrode on the side of μI is positively charged according to the reaction (12). The electrolyte layers on the side of μ_2 are depleted by cations. Excess oxygen leaves the electrolyte and charges the electrode negatively according to the reaction (13). In the process of diffusion of both anions and cations, oxygen is pumped towards its lower chemical potential, while the electric potential difference $\varphi(\tau)$ increases on the electrolyte, limiting diffusion. For an instantaneous value of the current density through an electrolyte of thickness h in the absence of redistribution of the volume charge, the expression can be written:

$$j(\tau) = \sum_{i=1}^{n} \frac{1}{h} \int_{0}^{h} \left[\sigma_{\mu i}(x,\tau) grad\mu(x,\tau) + \sigma_i(x,\tau) grad\varphi(x,\tau) \right] dx, \qquad (14)$$

where in square brackets is the current density of the i-th type of carriers in section x, under the sign of the sum is the average electrolyte current density of the i-th type of carriers.

Acknowledgements

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