Current Production Processes on Metallic Electrodes in Contact with Oxygen-Conducting Solid Electrolytes with Face-Centered Cubic Lattice of the Fluorite Type

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Abstract—The data concerning the processes of current production that occur in the electrode system \( \text{O}_2, \text{Pt}/\text{O}^{2-}\), which are available from relevant literature sources, are considered. Major progress in the understanding of the kinetics of an oxygen reaction has been attained with the application of model electrodes and cells, as well as at the expense of the application of such physical methods as a radiotracer method and atomic force microscopy. A discussion of model notions on the specific features of the occurrence of an oxygen reaction, which are formed on the basis of consideration of experimental results is the major subject matter of this communication. It is claimed that modernization of an existing model with allowance made for the fact of the existence, on the surface of an electrolyte with a face-centered cubic lattice, of a layer with another structure gives one a chance to also describe experimental results that cannot be described in the framework of an existing model.

Key words: oxygen-conducting solid electrolytes, model electrode

INTRODUCTION

All the existing oxides are characterized by some value of ion-oxygen conductance or another. We are aware of the existence of oxides, in which the share of an ion conductance is close to unity, and the value of the conductance itself does not appear to be unduly small. Such materials are called oxygen-conducting solid electrolytes (in what follows we will refer to these as OCSE). The very first of these electrolytes had been discovered by Nernst [1] as far back as in the XIX century. However, frankly speaking, the application of such electrolytes was begun only as late as in the mid of the XX century [2, 3]. For a long time the face-centered cubic (fcc) solid solutions with the structure of the fluorite type, whose first representative was a doped zirconium oxide, were the only class of OCSE that found any application at all. Starting with 1994 there became known one more type of OCSE, specifically, the electrolytes with the structure of the perovskite type [4, 5]. The oxygen-conducting solid electrolytes find broad application in such devices as sensors of the activity of oxygen, oxygen pumps and electrolyzers, and fuel cells. The unalienable part of all these devices is electrodes. The processes that occur on the electrodes in contact with the fcc OCSE had been actively studied during the last several decades. The biggest contribution to the development of notions concerning these electrode processes was made by collectives of scientists under the guidance of S. Karpachev and M. Perfil’ev (Sverdlovsk/Yekaterinburg, Russia) [6, 7] and M. Kleitz (Grenoble, France) [8, 9].

A BASE MODEL OR THE EXISTING NOTIONS ON THE OCCURRENCE OF ELECTRODE PROCESSES IN THE SYSTEM \( \text{O}_2, \text{METAL}/\text{O}^{2-} \) (SOLID ELECTROLYTE)

The full process that takes place on an electrode is described by the following expression:

\[
\frac{1}{2} \text{O}_2(\text{gas}) + V_0(\text{OCSE}) + 2e(\text{metal}) = O^x. \tag{1}
\]

In this expression symbol \( V_0 \) stands for an oxygen vacancy in an OCSE, and symbol \( O^x \) denotes an oxygen in its own position in an OCSE.

Components of three phases take part in process (1). This leads to the appearance of a certain specific region, which is called either a “triple-phase region” or a “triple-phase boundary.” For the very first time, the fact of the determining influence exerted by a triple-phase region was experimentally confirmed by A. Filyaev and S. Karpachev [10]. These researchers used a model platinum electrode, which approached an electrode of foil in its polarization characteristics. The authors of [10] measured the polarization characteristics of this initial sample and the characteristics of the same sample after depositing some scratches to its surface, that is after removing a portion of the electrode. Despite the

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The quality of contact may be monitored through transparent single crystal, as well as from the absence of the formation of bubbles in the course of anodic polarization. Item 3 is one of theauxiliary electrodes prepared from porous platinum and (4) is special construction glass, which possesses a coefficient of thermal expansion that coincides with both platinum and electrolyte and undergoes interaction with neither one nor the other.

Small; (ii) the current through the cell is proportional to the pressure of oxygen above the single crystal of the electrolyte to a power of 0.25. The existence of a deviation from this dependence points to the presence of leakage at the expense of a crack in the crystal or the glass, which may be removed; and (iii) the stationary current of the cell \(I\) increases with decreasing thickness of the crystal \(l\) (electrolyte was polished off step by step in the course of performing the measurements). In so doing, there is observed a linear dependence between the cell’s resistance and its thickness \(l\). Frankly speaking, however, these straight lines are not always extrapolated to zero, cutting a certain additional polarization resistance caused by some processes that occur at the gas/electrolyte interface.

A linear dependence of the resistance of the cell on the thickness of the cell points to that it is precisely the diffusion transport of minority charge carriers (electrons and holes) in the electrolyte that largely defines the overvoltage of a cell of the Hebb–Wagner type.

The results of the investigations on a cell of the Hebb–Wagner type lead to an understanding of that an electrode process that occurs at the expense of the participation of the electron subsystem of the electrolyte includes three steps. One step is the process of injection of electron charge carriers into the electrolyte

\[
e^-(\text{metal}) + h^+ (\text{electrolyte}) = \varnothing, \quad (2a)
\]

\[
e^- (\text{metal}) = e^- (\text{electrolyte}). \quad (2b)
\]

Another step involves the transport of the electron charge carriers away from the metal/electrolyte interface in the direction of the surface of the crystal of the electrolyte. And finally the third step consists of processes of the establishment of an equilibrium between the crystal of the electrolyte and a gas phase.

The first step in this chain of events had never been isolated as a limiting. Some roundabout estimates yield a quantity on the order of approximately \(10^{-4}\) ohm cm\(^{-2}\) for its partial polarization resistance at 800°C. The second step is the cause for the major portion of the overvoltage of a cell of the Hebb–Wagner type. This gives one a chance to determine the hole conductance of the electrolyte. For single crystals of the composition \(0.9\text{ZrO}_2–0.1\text{Y}_2\text{O}_3\) it is described by the relationship

\[
\sigma_h [\text{S cm}^{-1}] = 5.38 \times 10^2 (P_{O_2}/1\ \text{atm})^{0.25} \exp(-1.85\ \text{eV}/kT).
\]

If the stationary current through a cell is switched off, the electrolyte will return to a state of equilibrium with a gas phase. A solution for a time dependence of the emf of a cell [16] after the current is switched off allows one to calculate the diffusion coefficient for holes. For single crystals of the composition \(0.9\text{ZrO}_2–0.1\text{Y}_2\text{O}_3\) it is described by the relationship \(D_h [\text{cm}^2 \text{s}^{-1}] = 0.22\exp(-120 \pm 2 [\text{kJ mol}^{-1}]/kT)\).

The third step, which consists of processes of the establishment of equilibrium between the crystal of an