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Innovative oxide materials for electrochemical energy conversion and oxygen separation

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I. Introduction

Continuous increase in electricity production by combustion of fossil fuels led to severe environment pollution and depletion of natural resources. According to International Energy Agency (IEA) and other informed circles, fossil fuels will remain the main energy source until the mid-21st century. In this connection, the role of alternative energy sources (nuclear energy, solar energy, wind energy, hydroelectric energy and biomass energy) increases. Traditionally, electrochemical power engineering is of great importance. Electromechanical methods for power generation and electric energy storage are efficient and environmentally friendly. In the nearest future, the energy market share of such electrochemical devices as fuel cells, batteries, accumulators, oxygen separators, electrolyzers, etc. will increase. Progress in electrochemical power engineering will be to a great extent determined by advances in functional materials. In this connection, a particular role is assigned to oxygen-ion-conducting oxide materials.

At present, the most intensive research avenues include ceramic oxide materials for intermediate- and low-temperature solid-oxide fuel cells and ion transport membranes, as well as liquid oxide materials for intermediate-temperature molten oxide fuel cells and molten oxide membranes. Molten oxide fuel cells represent a novel type of fuel cells for electrochemical energy conversion; they combine the advantages of solid-oxide (air as cathode gas) and molten carbonate (highly conductive liquid electrolyte) fuel cells. Molten oxide membranes represent an innovative type of ion transport membranes for separation of ultrahigh-purity oxygen from air.

A molten oxide material is a composite consisting of solid grains and liquid channels at grain boundaries that form the so-called liquid-channel grain-boundary structure (LGBS). Intergranular liquid channels provide the molten oxide material with high ionic conductivity, gas tightness and ductility. The LGBS molten oxide materials are usually prepared in two steps, viz., by sintering a ceramic composite of specified composition followed by the formation of the LGBS in the ceramic composite by grain boundary wetting. Simple methods for preparation and unique electrochemical and mechanical properties of such materials offer great prospects for technological applications. The LGBS with high mixed ionic-electronic conductivity was for the first time found in the oxide layer formed on copper surface during catastrophic oxidation of copper contacting a low-melting oxide. Accelerated transport of oxygen ions along
intergranular liquid channels led to catastrophic degradation of the metal.

Recently, there has been visible progress in understanding the mechanism of oxygen ion transport in molten oxides. This was facilitated by the following two factors:
— improvement of experimental methods in order to perform highly accurate measurements of oxygen permeability in chemically harsh molten oxides at different temperatures and partial pressures of oxygen; and
— constructing models for correct description of oxygen ion transport in molten oxides.

The development of ideas about the mechanisms of oxygen ion transport in molten oxides makes it possible to design new-generation electrochemical materials and thus improve the efficiency of devices for electrochemical energy conversion and oxygen separation. The aim of this review is to integrate the results of experimental and theoretical research into the title field obtained in the last decade with particular attention paid to chemical diffusion of oxygen in molten oxides.

II. Thermodynamics of molten oxide materials

II.1. Wetting of grain boundaries

The preparation of molten oxide materials includes sintering of ceramic composites followed by the formation of the LGBS (see above). Usually, the LGBS is formed in binary oxide systems described by simple eutectic phase diagrams. To prepare a ceramic composite, a two-phase powder mixture of specified composition is pressed and sintered at a temperature below the eutectic point. Then, the sintered ceramic composite is heated above the eutectic temperature (two-phase region of a corresponding phase diagram, where the solid and liquid phases are in equilibrium). As the ceramic composite is heated at the eutectic temperature, a grain boundary wetting transition occurs and the LGBS is formed, i.e., a molten oxide material with the LGBS is formed. The material consists of solid grains and liquid intergranular channels. Wetting plays an important role in the fabrication of molten oxide materials and we will consider the phenomenon in more detail. Let us describe wetting using Young’s equation

\[ \gamma_{gb} = \gamma_{sa} + \gamma_{bg} \cos \theta \]  

(1)

where \( \gamma_{sa} \), \( \gamma_{bg} \), and \( \gamma_{gb} \) are the specific energies at the solid/gas, solid/liquid and liquid/gas interfaces, respectively, and \( \theta \) is the contact angle. The angle \( \theta \) varies around zero at the wetting transition; therefore, wetting is referred to as a critical phenomenon. Cahn \(^{23}\) showed that the wetting transition occurs in the vicinity of the critical point. He considered a two-component liquid \( \tau + \beta \) contacting a solid phase \( \gamma \); in such a liquid, the two-phase region is confined by the binodal \( \text{APCF} \text{A'} \) with a critical point \( C \) (Fig. 1). At \( T \rightarrow T_c \), the interface energy \( \gamma_{gb} \) decreases faster than the interface energy difference \( \gamma_{gb} - \gamma_{gb}^{\text{crit}} \). Consequently, there exists the temperature \( T_0 \) such that a liquid film of the \( \beta \)-phase is formed between the vessel wall \( \gamma \) and the liquid phase \( \tau + \beta \) above \( T_0 \); in other words, a wetting transition \( (\text{PP} \text{P'} \text{P} \text{P} \text{P}) \) occurs at the temperature \( T_0 \). Cahn also showed that the liquid film of the \( \beta \)-phase can exist outside the two-phase region \( \tau + \beta \) (between the line \( \text{PP} \text{P'} \text{P} \text{P} \text{P} \) and the binodal segment \( \text{PC} \) in Fig. 1). Cahn’s theory \(^{24}\) was many times confirmed experimentally.

![Figure 1. Solubility diagram of a binary system with a limited mutual solubility of components.](image)
$0.5 \leq \gamma_{\alpha/\beta} \leq 75 \text{ mJ} \text{ m}^{-2}$. Note that these $\gamma_{\alpha/\beta}$ values are typical of lyophilic colloidal systems.$^{37}$

The aforesaid suggests that wetting of grain boundaries in oxide ceramic composites with a chemically compatible liquid can occur in the two-phase region of corresponding phase diagram, where the solid and liquid phases are in equilibrium. The grain boundary energies vary over a wide range; therefore, the wetting transition temperature will also be different, namely, the lower the grain boundary energy the higher the wetting transition temperature and vice versa.

II.2. Intergranular wetting films

Clarke$^{38}$ evaluated the equilibrium thickness of intergranular wetting films in ceramic materials. He proposed two approaches within the framework of continuum approximation. One of them is based on evaluation of the grain boundary energies while the other is based on the balance of forces acting along the normal to the grain boundary. The results obtained suggest the existence of a stable thickness ($h \approx 1 \text{ nm}$, Fig. 2) of the intergranular film. According to Clarke, the equilibrium thickness of intergranular wetting film depends on two competing forces, that is, attractive force due to van der Waals dispersion interaction between grains, which tends to decrease the thickness of the intergranular liquid film, and repulsive force due to the structural (or steric) force of the liquid.

![Figure 2. The boundary phase $\beta$ of thickness $h$ between the phases $\alpha$ and $\gamma$. A schematic.](image)

In other words, the equilibrium thickness of an intergranular wetting film is governed by the balance between the long-range and short-range forces. The corresponding balance equation can be written as follows:

$$P + P_c + \Pi = 0$$

where $P$ is the external pressure, $P_c$ is the capillary pressure and $\Pi$ is the disjoining pressure (the total pressure due to all interfacial forces acting across the liquid intergranular film$^{39,40}$). To a first approximation, the disjoining pressure is represented by the sum

$$\Pi = \Pi_{\text{disp}} + \Pi_{\text{sr}}$$

where $\Pi_{\text{disp}}$ is the contribution of the van der Waals dispersion forces and $\Pi_{\text{sr}}$ is that of the structural or steric forces. Thus, the equation for the total normal force acting across the liquid intergranular film has the form

$$P + P_c + \Pi_{\text{disp}} + \Pi_{\text{sr}} = 0$$

II.2.a. The dispersion force

In the interaction between individual atoms or molecules the dispersion force is inversely proportional to the seventh power of the interatomic (intermolecular) distance, thus being short-range. The force of dispersion interaction between bulk solid phases is long-range.$^{41}$ In order to calculate the London dispersion force acting between two interacting phases separated by a third phase, Dzyaloshinski et al.$^{42}$ used an approach based on the Lifshitz quantum field theory and led to the following equation:

$$\Pi_{\text{disp}} = \frac{\hbar}{8\pi \varepsilon_0^2} \sum_{\alpha\beta} \int_0^\infty \sum_{n=1}^\infty \frac{1}{n^2} \left( \frac{\varepsilon_\alpha - \varepsilon_\beta}{\varepsilon_\alpha + \varepsilon_\beta} \right)^{\frac{1}{n}} \left( \frac{\varepsilon_\gamma - \varepsilon_\alpha}{\varepsilon_\gamma + \varepsilon_\alpha} \right)^{\frac{1}{n}} \frac{d\xi}{\xi}$$

(8)

where $\varepsilon_j = \varepsilon_j(i\xi)$ is the dielectric constant of the $j$th phase, which depends on the imaginary frequency $i\xi$, and $\hbar$ is the Planck constant.

Equation (8) shows that the dispersion force can be either attractive or repulsive depending on the dielectric constants of the three phases under study (repulsive dispersion force acts if $\varepsilon_\alpha > \varepsilon_\beta > \varepsilon_\gamma$, see Fig. 2). In our case (same-phase grains, i.e., $\varepsilon_\alpha = \varepsilon_\beta$), Eqn (8) is simplified:

$$\Pi_{\text{disp}} = \frac{\hbar}{8\pi \varepsilon_0^2} \sum_{\alpha\beta} \int_0^\infty \sum_{n=1}^\infty \frac{1}{n^2} \left( \frac{\varepsilon_\alpha - \varepsilon_\beta}{\varepsilon_\alpha + \varepsilon_\beta} \right)^2 \frac{d\xi}{\xi} = H_{\text{disp}} 6\pi\eta h$$

(9)

where $H_{\text{disp}}$ is the Hamaker constant. In this symmetrical case, the dispersion force is attractive irrespective of the nature of the grain boundary material.

Therefore, if no external stress is applied to the system and in the absence of capillary pressure, thin intergranular films are unstable against the attractive force due to the dispersion interaction unless there exists a repulsive steric force of sufficient strength to balance the long-range van der Waals force.

II.2.b. The structural component of the disjoining pressure

Taking account of the fact that the structure of the intergranular liquid film of microscopically small thickness is characterized by fluctuating orientational order near each crystalline grain (epitaxy) and using the mean field approximation where orientational ordering across the grain boundary is described by a scalar quantity $\sigma_0(x)$, Clarke$^{38}$ proposed to determine the free energy density ($g$) of the liquid phase as a Taylor expansion

$$g = g_0 + [a\sigma_0^2(x) + b\sigma_0^4(x) + c\sigma_0^6(x) + \ldots] + \lambda \left( \frac{d\sigma_0(x)}{dx} \right)^2$$

(10)

This expression is known as the Ginzburg–Landau or Cahn–Hilliard equation$^{43,44}$ and includes three dominant terms. The first, $g_0$, is the free energy density of bulk random liquid; the second term is a power series expansion of the order parameter $\sigma_0$ (Landau expansion); and the third term, the so-called gradient energy, describes the contribution due to the interaction between adjacent molecules. From the symmetry of the grain-boundary region and, therefore, the order parameter, it follows that $b = 0$. The constant $c$ is small compared to $a$ so that the term $c\sigma_0^4$ can be neglected. As a result, Eqn (10) is simplified and one gets

$$g = g_0 + a\sigma_0^2(x) + \lambda \left( \frac{d\sigma_0(x)}{dx} \right)^2$$

(11)
The functional of the excess free energy per unit area of grain boundary is given by

$$\Delta G = \int_{-h/2}^{+h/2} (g - g_0) dx$$

(12)

After the function minimizing this functional ($\Delta G_{eq}$) has been defined, the structural contribution to the disjoining pressure is calculated using the equation

$$\Pi_a = \frac{d(\Delta G_{eq})}{dh}$$

(13)

To determine the equilibrium thickness of the intergranular liquid film, one should establish the conditions under which the excess free energy functional is minimum. One has to solve the following equation:

$$\Delta G_{eq} = 2 \sqrt{(a \xi)} \eta_0 \cosh \left( \frac{\sqrt{a/\zeta} h}{2} \right)$$

(14)

provided that crystalline grains are misoriented in such a manner that the first monolayers of the liquid film are oriented in opposite directions, i.e.,

$$\omega_h = \frac{h}{2} = -\omega \left( -\frac{h}{2} \right)$$

(14a)

Substituting Eqn (14) into formula (13), one gets the expression for the disjoining pressure:

$$\Pi_a = \frac{d(\Delta G_{eq})}{dh} = -\frac{\phi_0}{sh^2(h/2\zeta)}$$

(15)

where $\phi_0 = a \omega_0^2$ and $\zeta = \sqrt{\lambda/a}$ is the correlation length. At $h > \zeta$, the contribution of the disjoining pressure can be evaluated using the expression

$$\Pi_a = -4\phi_0 \exp \left( -\frac{h}{\zeta} \right)$$

(16)

This model predicts a repulsive character of the structural disjoining pressure, as required to balance the attractive intergranular force originated from the van der Waals dispersion interaction. Substituting Eqns (9) and (16) into Eqn (7), one gets the equation of balance in the form

$$P + P_c + \frac{H_{\text{dil}}}{6\pi h^3} - 4\omega_0^2 \exp \left( -\frac{h}{\zeta} \right) = 0$$

(17)

The equilibrium thickness of the intergranular liquid film can be determined from

$$\frac{H_{\text{dil}}}{6\pi h^3} = 4\omega_0^2 \exp \left( -\frac{h}{\zeta} \right)$$

(18)

Using the continuum approach based on the balance of forces acting along the normal to the intergranular liquid film, Clarke showed that such films may have the equilibrium thickness. The thickness of the intergranular film calculated using formula (18) is close to experimental data ($\sim 1$ nm). However, this contradicts the data reported by Derjaguin, who demonstrated that on the length scale less than 1.5 nm the continuum approach is of limited use and therefore quantitative estimates are not reliable. Besides, experiments with ceramic materials confirmed the existence of intergranular wetting films whose thickness much exceeds that predicted by Clarke (Fig. 3). Note that the nature of the nanometre-thick intergranular films in ceramic materials is unclear at the moment. Thus, one should clarify whether such films are truly wetting, prewetting or adsorption ones.

In conclusion, recall that grain boundary wetting transitions and formation of the LGBS can occur in ceramic oxide composites at the eutectic point. Intergranular liquid channels provide the molten oxide materials with LGBS high ionic conductivity, gas tightness and ductility. As will be shown below, such a combination of unique properties of these materials offers great prospects for their application in electrochemical devices for power generation and production of oxygen.

III. Molten oxide layer on metal. Catastrophic oxidation of copper

The LGBS with high oxygen ion conductivity was for the first time discovered in the oxide layer formed on copper surface during catastrophic oxidation of copper contacting low-melting oxides Bi$_2$O$_3$, V$_2$O$_5$ or MoO$_3$. Rapid transport of oxygen along intergranular liquid channels led to catastrophic degradation of the metal. However, rapid mass transfer can be successfully used in practice electrochemical devices such as molten oxide fuel cells and molten oxide membranes. Therefore, studies on the mechanism of the catastrophic oxidation of metals are of importance for the design of innovative molten oxide LGBS materials with high oxygen ion conductivity. Accelerated oxidation of metals and alloys due to formation of a liquid corrosion product has been widely discussed in the literature. Consider the mechanism of catastrophic oxidation of copper taking the best studied system Cu – Bi$_2$O$_3$ as an example.

The catastrophic oxidation of copper coated with a Bi$_2$O$_3$ layer includes two stages, a fast and a superfast one. The fast stage is realized under a thin (10–100 µm) Bi$_2$O$_3$ layer and proceeds by the diffusion mechanism, while the superfast stage is realized under a thick (>1 cm) Bi$_2$O$_3$ layer and proceeds by the fluxing
mechanism. Since in the text below we will only be interested in the diffusion mechanism, consider the fast stage of the process in question. It was established that copper plates coated with a thin Bi₂O₃ layer undergo catastrophic oxidation at 1043 K. The kinetics of the process at different thickness of the Bi₂O₃ layer is shown in Fig. 4. The catastrophic oxidation of copper obeys a parabolic rate law and, therefore, is diffusion-controlled

\[
\frac{(m/S)^2}{kg^2 m^{-4}} = k' t
\]

where \( m \) is the change in the mass of the oxide layer growing on the metal, \( S \) is the surface area of the copper plates, \( k' \) (kg\(^2\) m\(^{-4}\) s\(^{-1}\)) is the parabolic rate constant, and \( t \) is time.

Equation (19) is used only if the mass of the growing oxide layer is controlled. If the thickness of the growing layer is measured, another equation is used:

\[
h^2 = 2k' t
\]

where \( h \) is the thickness of the oxide layer growing on the metal and \( k' \) is the parabolic rate constant (m\(^2\) s\(^{-1}\)).

The oxide layer formed on the copper surface during the catastrophic oxidation process consists of Bi₂CuO₄, CuO, Cu₂O and Bi₂O₃.⁴⁵ According to the phase diagram of the Bi₂O₃ – CuO system,⁶³,⁶⁴ the threshold temperature (1043 K) of the catastrophic oxidation of copper coincides with the Bi₂CuO₄ – Bi₂O₃ eutectic point. A grain boundary wetting transition and formation of the LGBS in Bi₂CuO₄ – Bi₂O₃ ceramic composites at 1043 K was confirmed experimentally (Fig. 5). Thus, the catastrophic oxidation of copper is related to the formation of the LGBS in the oxide layer.

Studies on the electrochemical properties of LGBS ceramic composites Bi₂CuO₄ – (5 - 20) mass % Bi₂O₃ showed that they are mixed ionic-electronic conductors in which solid Bi₂CuO₄ grains conduct electrons while inter-

granular liquid channels predominantly conduct oxygen ions.⁶⁵,⁶⁶ The ionic conductivity of the composites increases with increasing volume fraction of the liquid phase (Fig. 6). This suggests that the molten oxide layer with the larger volume fraction of the liquid phase, formed on the copper surface, also has a higher oxygen ion conductivity than the oxide layer with the lower content of the liquid phase and, therefore, higher rate of catastrophic oxidation, which was also confirmed experimentally (see Fig. 4).

Consider a theory of the catastrophic oxidation of copper under a thin layer of a low-melting oxide.⁶⁷

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Figure 4. Kinetics of catastrophic oxidation of copper plates (20 x 20 x 0.4 mm) coated with a Bi₂O₃ layer of different thickness at 1073 K.⁴⁵
Film thickness \(10^{-5} m\): 0.2 (1), 3 (2), 6 (3), 9 (4); \(10^3 k'/kg^2 m^{-4} s^{-1}\): 0.012 (1), 1.6 (2), 4.9 (3), 21 (4).

Figure 5. Microstructure (fracture face) of the molten oxide LGBS composite Bi₂CuO₄ — 20 mass % Bi₂O₃ after cooling from 1053 K.⁴⁵
General view (a) and intergranular channel (b).

Figure 6. Oxygen ion conductivity of the molten oxide LGBS composites Bi₂CuO₄ – 5 mass % Bi₂O₃ (1), 10 mass % Bi₂O₃ (2), 15 mass % Bi₂O₃ (3), 20 mass % Bi₂O₃ (4) plotted vs. volume fraction of the liquid phase (\(\eta\)) at 1073 K.⁶⁷
model structure of the oxide layer used in developing the theory is shown in Fig. 7. The theory was developed under the following assumptions:

— the LGBS is formed in the oxide layer;
— intergranular liquid channels act as pathways for oxygen ion transport;
— the oxidation rate is controlled by the diffusion of oxygen ions;
— oxygen ions and electrons are the most mobile charge carriers;
— transport of ions and electrons across the oxide layer occurs in such a manner that the total electric current is zero;
— a steady state is established throughout the oxide layer;
— the solubility of oxygen in copper is neglected; and — the thickness of the oxide layer is large compared to the distances at which the space charge effects manifest themselves.

If the oxygen concentration in the oxide layer is designated by \( c \) and the layer thickness at instant \( t \) is designated by \( h \) (see Fig. 7), the mass balance equation takes the form:

\[
\frac{dh}{dt} = j_{O_2}
\]  

where \( j_{O_2} \) is the oxygen flux through the molten oxide LGBS layer. Usually, diffusion-controlled oxygen flux is described by the Wagner equation. In our case, the action of the chemical potential gradient causes oxygen ions to migrate towards regions with reduced partial pressure of oxygen \( (P'_{O_2} > P''_{O_2}, \text{ i.e.}, \text{through the oxide layer towards the metal}) \). Since oxygen ions are charged, such a migration will produce an electric field and subsequent transport of electrons through the oxide layer in the opposite direction. The relative migration rates of oxygen anions and electrons are balanced, so the total charge transferred through the oxide layer is zero. Charged species (oxygen ions) respond to both the chemical potential gradient and the electric potential gradient. Joint action of these gradients provides the driving force of ion migration, that is, the electrochemical potential gradient. Consider an ion bearing the charge \( z \).

At a point characterized by the chemical potential gradient \( \frac{\partial \mu}{\partial x} \) and the electric potential gradient \( \frac{\partial \varphi}{\partial x} \), the ion experiences the electrochemical force (\( Q \))

\[
Q = \frac{1}{N_A} \frac{d\mu}{dx} + zF \frac{\partial \varphi}{\partial x}
\]  

where \( N_A \) is the Avogadro constant and \( e \) is the electron charge. The ion moving under the action of a constant force acquires a constant drift velocity. The stabilized drift velocity of the ion under the action of a unit force is characterized by the mobility \( (B) \) of a species. Therefore, the oxygen ion flux \( j_i \) (mol m\(^{-2}\) s\(^{-1}\)) is given by

\[
\dot{j}_i = \frac{c_i B_i}{e z_i e} \left( \frac{d\mu}{dx} + z_i F \frac{\partial \varphi}{\partial x} \right)
\]  

where \( c_i \) is the concentration of oxygen ions, \( B_i \) is the mobility of oxygen ions and \( F \) is the Faraday constant. The mobility is related to the ionic conductivity \( (\sigma_i) \):

\[
B_i = \frac{\sigma_i}{e z_i e}
\]  

Substituting Eqn (24) into Eqn (23), one gets the expression for the ion flux:

\[
\dot{j}_i = \frac{\sigma_i}{e z_i e} \left( \frac{d\mu}{dx} + z_i F \frac{\partial \varphi}{\partial x} \right)
\]  

Correspondingly, for the electron flux \( j_e \) one has

\[
\dot{j}_e = \frac{\sigma_e}{e z_e e} \left( \frac{d\mu}{dx} + z_e F \frac{\partial \varphi}{\partial x} \right)
\]  

where \( \sigma_e \) is the electronic conductivity. The electrical neutrality condition has the form

\[
z_i \dot{j}_i = z_e \dot{j}_e
\]  

Using Eqns (25)–(27), one can express \( \frac{\partial \varphi}{\partial x} \)

\[
\frac{\partial \varphi}{\partial x} = \frac{1}{\sigma_i + \sigma_e} \left( \frac{\sigma_i d\mu}{dx} + \frac{\sigma_e d\mu}{dx} \right)
\]

Substituting Eqn (28) into Eqn (25) gives the expression for the oxygen ion flux:

\[
\dot{j}_i = \frac{\sigma_i \sigma_e}{e z_i e} \left( \frac{d\mu}{dx} + \frac{\sigma_e d\mu}{dx} \right)
\]  

Taking account of the electron charge \( (z_e = -1) \) and oxygen ion charge \( (z_i = -2) \), Eqn (29) can be transformed to

\[
\dot{j}_i = \frac{\sigma_i \sigma_e}{4F^2(\sigma_i + \sigma_e)} \left( \frac{d\mu_i}{dx} + \frac{\sigma_e d\mu_e}{dx} \right)
\]

Using the dissociation equation

\[
\frac{1}{2} O_2 \rightarrow O^2^- - 2e^- \tag{30a}
\]
the chemical potential oxygen is
\[ \frac{1}{2} \mu_{O_2} = \mu_i - 2\mu_e \] (31)
Thus, the oxygen ion flux across the oxide layer can be written in the form
\[ j = \frac{\sigma_i \sigma_e}{8F^2(\sigma_i + \sigma_e)} \frac{d\mu_{O_2}}{dx} \] (32)
where \( \sigma_i, \sigma_e \) and \( d\mu_{O_2}/dx \) are the instantaneous values at a given point of the oxide layer. Since they may vary from one point to another, it is necessary to integrate Eqn (32)
\[ j_{O_2} = \frac{1}{2} h = \frac{1}{16F^4h} \int \sigma_{amb} d\mu_{O_2} \] (33)
where \( j_{O_2} \) is the oxygen flux, \( h \) is the thickness of the LGBS oxide layer, \( \sigma_{amb} \) is the ambipolar conductivity of oxygen ions and electrons in the oxide layer
\[ \sigma_{amb} = \frac{\sigma_i \sigma_e}{\sigma_i + \sigma_e} \] (34)
The chemical potential of oxygen, \( \mu_{O_2} \), is related to the partial pressure of oxygen \( P_{O_2} \):
\[ \mu_{O_2} = \mu^*_{O_2} + RT \ln P_{O_2} \] (35)
where \( \mu^*_{O_2} \) is the standard chemical potential of oxygen, \( R \) is the universal gas constant and \( T \) is temperature. Substituting Eqn (35) into Eqn (33), one gets
\[ j_{O_2} = \frac{RT}{16F^4h} \sigma_{amb} \ln \frac{P'_{O_2}}{P''_{O_2}} \] (36)
where \( P'_{O_2} \) and \( P''_{O_2} \) is the partial pressure of oxygen at the air/oxide layer and oxide layer/copper interfaces, respectively (see Fig. 7). Using the average value \( \sigma_{amb} \), we get
\[ j_{O_2} = \frac{RT}{16F^4h} \sigma_{amb} \ln \frac{P'_{O_2}}{P''_{O_2}} \] (37)
If \( \sigma_e \gg \sigma_i \), Eqn (37) is transformed to
\[ j_{O_2} = \frac{RT}{16F^4h} \sigma_i \ln \frac{P'_{O_2}}{P''_{O_2}} \] (38)
The parabolic temporal law of oxidation has the form
\[ \frac{dh}{dt} = \frac{k'}{h} \] (39)
Here \( k' \) (m² s⁻¹) is the parabolic rate constant related to \( k'' \) (kg² m⁻⁴ s⁻¹) as follows:
\[ k' = \frac{V^2}{2A^2} k'' \] (40)
where \( V \) is the molar volume of the oxide layer and \( A \) is the atomic mass of oxygen. Using Eqns (21), (38), (39) and (40), the rate constant \( k'' \) can be expressed as
\[ k'' = \frac{RT^2 \sigma_i^2}{8F^2 V^2 e^2} \ln \frac{P_{O_2}}{P'_O} \] (41)
The rate constants \( k'' \) calculated using expression (41) are in the range between 2.0 × 10⁻⁵ and 4.9 × 10⁻⁴ kg² m⁻⁴ s⁻¹ (\( T = 1073 \) K, \( A^2 = 2.6 \times 10^{-6} \) kg² mol⁻², \( V^2 = 1.5 \times 10^{-10} \) m⁶ mol⁻², \( c = 4.0 \times 10^{4} \) mol m⁻³, \( P_{O_2} = 0.021 \) MPa, \( P''_{O_2} = 0.0001 \) MPa, \( \sigma_i = 0.14 \) and 3.6 S m⁻¹) and coincide in order of magnitude with experimental data (\( k'' = 1.6 \times 10^{-5} - 2.1 \times 10^{-4} \) kg² m⁻⁴ s⁻¹) (see Fig. 4); this indicates a reasonable agreement between theory and experiment.

It should be noted that the mixed-conducting molten oxide LGBS layer found on the copper surface during the catastrophic oxidation of copper20 served a prototype for the design of novel molten oxide membranes with high mixed oxygen-ion-electronic conductivity.68

IV. Molten oxide membranes

IV.1. Materials

Wagner69 was the first who considered mixed ionic-electronic conductors as practically attractive. If a mixed-conducting material is placed between two gas-filled compartments that differ in the partial pressure of oxygen, the material can act as oxygen separation membrane. More recently, ten Elshof et al.70 proposed a perovskite-related mixed conductor Sr(Fe,Co)O₃₋₁ that acts as membrane material. Bouwmeester and Burggraaf,71 as well as Peca and Fierro72 compiled the results of studies on perovskite-related mixed-conducting membrane materials. Mazanec et al.73 proposed a concept of a two-phase oxygen-permeable composite material. High mixed ionic-electronic conductivity was discovered in the solid electrolyte/noble metal cermet. Cerments YSZ/Pd (where YSZ is yttria-stabilized zirconia),74 GDC/Pd (where GDC is gadolinium-doped ceria),75 GDC/Ag,76 Bi₂O₃₋₁Er₂O₃₋₁/Ag (Ref. 77 and 78) are characterized by rather high oxygen permeability. Also, high oxygen permeability was demonstrated by the ceramic composites δ-Bi₂O₃–In₂O₃ and δ-Bi₂O₃–NiO prepared by in situ crystallization of molten Bi₂O₃.79,80 Ce₀.₈Gd₀.₂O₂₋₁–Fe₂CoO₄ (Ref. 81) and Ce₀.₈Sm₀.₂O₂₋₁–SrCo₁₋ₓCeₓO₄ (Ref. 82). Small amounts of transition metal oxides added to a molten slag also significantly improve the oxygen permeability of the slag.83–85

Recently, high oxygen permeability of molten oxide LGBS composites based on Bi₂O₃ and V₂O₅ has been reported.86 These materials seem to be promising as molten oxide membranes68 for ultrahigh purity oxygen separators. Molten oxide membrane materials can be divided into two groups. One of them contains molten Bi₂O₃ while the other contains molten V₂O₅. High oxygen ion conductivity of these oxides in the molten state was confirmed experimentally.87 The first group includes the systems NiO–Bi₂O₃, In₂O₃–Bi₂O₃, Co₃O₄–Bi₂O₃, ZnO–Bi₂O₃ and CuO–Bi₂O₃; the second group includes ZrO₂–V₂O₅ and Bi₂O₃–V₂O₅. These membrane materials consist of electron-conducting solid grains (dark areas in Figs 8 and 9) and intergranular liquid channels with predominant oxygen ion conductivity (light areas in Figs 8 and 9). Intergranular
liquid channels provide the membrane material with high
ionic conductivity, gas tightness and ductility (Fig. 10).

IV.2. Electrical conductivity
A number of molten oxide LGBS materials exhibit high
mixed ionic-electronic conductivity. The temperature
dependence of the conductivity of the composite
Co$_3$O$_4$–36 mass % Bi$_2$O$_3$ is shown in Fig. 11. A large
contribution to the total conductivity of the composite comes
from Co$_3$O$_4$. According to published data, the non-
linear temperature dependence of the conductivity of this
composite is due to partial structural transition of Co$_3$O$_4$
from the normal to the inverse spinel; this seems to be due
to the change in the state of electron spins in Co$^{3+}$ (from
the low-spin to the high-spin configuration). At 1953 K, a
grain boundary wetting transition occurs and the LGBS is
formed. Measurements of the oxygen ion transport
number in the molten oxide LGBS composite
Co$_3$O$_4$–36 mass % Bi$_2$O$_3$ in the temperature interval
1053–1123 K showed that the material exhibits both elec-
tronic conductivity and oxygen ion conductivity, thus being
a mixed ionic-electronic conductor.

The conductivity and oxygen ion transport number of
the molten oxide LGBS composites Bi$_2$CuO$_4$–Bi$_2$O$_3$ at
1053 K at different average Bi$_2$CuO$_4$ grain size are listed
in Table 1. As can be seen, the smaller the grain size the
higher the ionic conductivity of the composites. Such a
correlation can be explained by the contribution of the solid
oxide/liquid oxide interfaces to the ionic conductivity of the
composites.

The temperature dependences of conductivity of com-
posites ZnO–Bi$_2$O$_3$ are shown in Fig. 12. From the phase
diagram of the system ZnO–Bi$_2$O$_3$ (Refs 92 and 93) it
follows that a low-conductive phase Bi$_{38}$ZnO$_{58}$ with the
sillenite structure exists in the temperature interval
873–1026 K and, therefore, the major contribution to the
conductivity comes from ZnO. An increase in conductiv-
ity at 1026 K is due to the grain boundary wetting transition
and formation of the LGBS. The oxygen ion transport
number and the conductivity of the molten oxide LGBS
composites ZnO–Bi$_2$O$_3$ increase with increasing volume
fraction of the liquid phase ($\eta$) (Fig. 13).

The conductivity of the composites NiO–Bi$_2$O$_3$ and
In$_2$O$_3$–Bi$_2$O$_3$ is plotted
vs. temperature in Fig. 14. The

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**Figure 8.** Microstructure (fracture face) of the molten oxide LGBS composite Co$_3$O$_4$–36 mass % Bi$_2$O$_3$ after cooling from 1123 K.$^{17}$

**Figure 9.** Microstructure (fracture face) of the molten oxide LGBS composite In$_2$O$_3$–30 mass % Bi$_2$O$_3$ after cooling from 1073 K.$^{19}$

**Figure 10.** Photograph of the starting ceramic composite ZnO–30 mass % Bi$_2$O$_3$ (a) and the molten oxide LGBS composite ZnO–30 mass % Bi$_2$O$_3$ after deformation at 1073 K (b).$^{19}$

**Figure 11.** Conductivity of Co$_3$O$_4$ (1), Co$_3$O$_4$–6 mass % Bi$_2$O$_3$ (2) and Bi$_2$O$_3$ (3) plotted vs. temperature.$^{17}$ Curves 1 and 3 are shown for comparison.
electronic conductivity of In$_2$O$_3$ and the hole conductivity of NiO are most pronounced in the temperature interval 773 – 1003 K. The conductivity jump at 1003 K is due to the polymorphic transformation \( \alpha \)-Bi$_2$O$_3 \rightarrow \delta \)-Bi$_2$O$_3$, which is accompanied by a significant increase in the oxygen ion conductivity. Considerable intrinsic disorder and high mobility of oxygen ions are in agreement with the

<table>
<thead>
<tr>
<th>Composite</th>
<th>( t_i )</th>
<th>( \sigma_i )</th>
<th>( d )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$_2$CuO$_4$ – 10 mass % Bi$_2$O$_3$</td>
<td>0.03</td>
<td>0.22</td>
<td>20</td>
</tr>
<tr>
<td>Bi$_2$CuO$_4$ – 10 mass % Bi$_2$O$_3$</td>
<td>0.05</td>
<td>0.42</td>
<td>10</td>
</tr>
<tr>
<td>Bi$_2$CuO$_4$ – 15 mass % Bi$_2$O$_3$</td>
<td>0.14</td>
<td>1.26</td>
<td>20</td>
</tr>
<tr>
<td>Bi$_2$CuO$_4$ – 15 mass % Bi$_2$O$_3$</td>
<td>0.18</td>
<td>1.68</td>
<td>10</td>
</tr>
<tr>
<td>Bi$_2$CuO$_4$ – 20 mass % Bi$_2$O$_3$</td>
<td>0.26</td>
<td>2.91</td>
<td>20</td>
</tr>
<tr>
<td>Bi$_2$CuO$_4$ – 20 mass % Bi$_2$O$_3$</td>
<td>0.32</td>
<td>6.50</td>
<td>10</td>
</tr>
</tbody>
</table>

Figure 12. Conductivity of the molten oxide LGBS composites ZnO – Bi$_2$O$_3$ containing 15 mass % Bi$_2$O$_3$ (1), 20 mass % Bi$_2$O$_3$ (2), 25 mass % Bi$_2$O$_3$ (3) and 30 mass % Bi$_2$O$_3$ (4) plotted vs. temperature.

Figure 13. Oxygen ion transport number (a) and conductivity (b) of the molten oxide LGBS composites ZnO – Bi$_2$O$_3$ plotted vs. volume fraction of the liquid phase at different temperatures. Bi$_2$O$_3$ content (mass %): 15 (1), 20 (2), 25 (3) and 30 (4).

Figure 14. Conductivity of NiO – Bi$_2$O$_3$ (a) and In$_2$O$_3$ – Bi$_2$O$_3$ (b) composites plotted vs. temperature. Bi$_2$O$_3$ content (mass %): 100 (1), 48 (2), 42 (3), 36 (4), 30 (5) and 0 (6).
entropy and structure of $\delta$-$\text{Bi}_2\text{O}_3$. For instance, an increase in entropy upon the $\alpha$-$\text{Bi}_2\text{O}_3 \rightarrow \delta$-$\text{Bi}_2\text{O}_3$ transition is $\sim 75\%$ of the total increase in entropy upon transition of solid $\alpha$-$\text{Bi}_2\text{O}_3$ to the liquid state. Hence, the disorder and conductivity of solid $\delta$-$\text{Bi}_2\text{O}_3$ are almost comparable with those of liquid $\text{Bi}_2\text{O}_3$ and therefore the solid $\delta$-$\text{Bi}_2\text{O}_3 \rightarrow$ liquid $\text{Bi}_2\text{O}_3$ transition at 1093 K is not accompanied by a significant increase in the ionic conductivity.

The dependence of the oxygen ion transport number on the volume fraction of the liquid phase in the molten oxide LGBS composites NiO – $\text{Bi}_2\text{O}_3$ and In$_2$O$_3$ – $\text{Bi}_2\text{O}_3$ is presented in Fig. 15. In these systems, only the intergranular liquid channels conduct oxygen ions; therefore, the oxygen ion transport number increases as the volume fraction of the liquid phase increases. The aforesaid is also confirmed by the dependence of the conductivity of the molten oxide LGBS composites NiO – $\text{Bi}_2\text{O}_3$ and In$_2$O$_3$ – $\text{Bi}_2\text{O}_3$ on the volume fraction of the liquid phase (Fig. 16).

In conclusion, mention may be made that the molten oxide LGBS composites considered in this Chapter conduct both oxygen ions and electrons and can thus be used as ion...
transport membranes for oxygen separation from air. Rapid transport of oxygen through these composites under the action of electrochemical potential gradient is due to high ambipolar oxygen ion and electronic conductivity of these systems (Fig. 17).

IV.3. Gas permeability
Molten oxide LGBS membrane materials exhibit high oxygen permeability.68 Usually, oxygen transport occurs in three stages. The first stage involves dissociation of oxygen molecules into anions at the air/membrane material interface (see Fig. 17), also known as the surface exchange reaction.101, 102 In the second stage, oxygen anions migrate through the membrane material; this is the so-called coupled chemical diffusion. The third stage represents recombination of oxygen anions to molecules. Each stage can be rate-limiting for the oxygen transport through the membrane material. To establish the rate-limiting stage, the oxygen flux was measured at different thickness of the membrane material. If the rate of oxygen transport across the membrane is controlled by the chemical diffusion, the oxygen flux should be inversely proportional to the membrane thickness (at specified difference of the partial pressures of oxygen) in accordance with Eqn (37). Linear dependence between the oxygen flux and membrane thickness (in the experimental thickness interval of 0.1–0.3 cm) for the molten oxide LGBS membrane materials NiO–Bi2O3, In2O3–Bi2O3, Co3O4–Bi2O3 and ZrV2O7–V2O5 indicates that the oxygen transport rate in these materials is diffusion controlled.68 However, the dependence for the molten oxide LGBS membrane material BiVO4–V2O5 is nonlinear (Fig. 18). Consequently, the oxygen transport rate is limited by both chemical diffusion and surface exchange reactions (mixed control).101 In this case, the oxygen flux can be described by the equation

\[ j_0 = \frac{RT}{16F^2(h + 2k_e)} \sigma_{amb} \ln \left( \frac{P_{O_2}^j}{P_{O_2}^e} \right) \]

where \( h_e \) is the characteristic membrane thickness at which the oxygen transport rate is equally controlled by the coupled chemical diffusion and by the surface exchange reactions. The characteristic membrane thickness is defined as

\[ h_e = \frac{t_e D_i}{K} \]

Where \( t_e \) is the electron transport number, \( D_i \) is the diffusion coefficient of oxygen ions and \( K \) is the surface exchange coefficient of oxygen. Evaluation of the characteristic thickness of the molten oxide LGBS membrane material BiVO4–10 mass % V2O5 gave a value of about 0.07 cm.102 The curve calculated using expression (42) with \( h_e \approx 0.07 \text{ cm} \) and the experimental curve in Fig. 18 almost coincide in the thickness interval of 0.1–0.3 cm. A further decrease in the film thickness (< 0.07 cm) will lead to the situation where the oxygen transport rate will only be controlled by the surface exchange reactions.

Thus, the oxygen flux through the molten oxide LGBS membrane materials NiO–Bi2O3, In2O3–Bi2O3, Co3O4–Bi2O3 and ZrV2O7–V2O5 at 1023–1173 K is controlled by coupled chemical diffusion (in the experimentally used thickness interval of 0.1–0.3 cm). The exception is only the molten oxide LGBS membrane material BiVO4–V2O5 where the oxygen flux is controlled by both chemical diffusion and surface exchange reactions (mixed control). As applied to the molten oxide LGBS membrane materials, this is observed only at temperatures below 973 K.

\[ \text{Figure 18. Oxygen flux plotted vs. thickness of the molten oxide LGBS composite BiVO}_4–10 \text{ mass} \% \text{ V}_2\text{O}_5: \text{experimental data (1) and results of calculations using Eqn (42) (2) and Eqn (37) (3).102 log}\left( P_{O_2}^j/P_{O_2}^e \right) = 2.3, T = 923 \text{ K.} \]

where \( t_e \) is the electron transport number, \( D_i \) is the diffusion coefficient of oxygen ions and \( K \) is the surface exchange coefficient of oxygen. Evaluation of the characteristic thickness of the molten oxide LGBS membrane material BiVO4–10 mass % V2O5 gave a value of about 0.07 cm.102 The curve calculated using expression (42) with \( h_e \approx 0.07 \text{ cm} \) and the experimental curve in Fig. 18 almost coincide in the thickness interval of 0.1–0.3 cm. A further decrease in the film thickness (< 0.07 cm) will lead to the situation where the oxygen transport rate will only be controlled by the surface exchange reactions.

Thus, the oxygen flux through the molten oxide LGBS membrane materials NiO–Bi2O3, In2O3–Bi2O3, Co3O4–Bi2O3 and ZrV2O7–V2O5 at 1023–1173 K is controlled by coupled chemical diffusion (in the experimentally used thickness interval of 0.1–0.3 cm). The exception is only the molten oxide LGBS membrane material BiVO4–V2O5 where the oxygen flux is controlled by both chemical diffusion and surface exchange reactions (mixed control). As applied to the molten oxide LGBS membrane materials, this is observed only at temperatures below 973 K.

Table 2: Transport properties of ceramic and molten oxide membrane materials.

<table>
<thead>
<tr>
<th>Membrane material</th>
<th>T/K</th>
<th>( j_0 )/mol cm(^{-2}) s(^{-1})</th>
<th>h/mm</th>
<th>( P_{O_2}^j )/MPa</th>
<th>( P_{O_2}^e )/MPa</th>
<th>( \sigma_{amb} ) mol cm(^{-2})</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ceramic materials</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Pr(<em>{0.6})Sr(</em>{0.4})Co(<em>{0.5})Fe(</em>{0.5})O(_{3-\delta})</td>
<td>1173</td>
<td>2.3 \times 10(^{-7})</td>
<td>0.6</td>
<td>0.021</td>
<td>0.0001</td>
<td>2.6 \times 10(^{-9})</td>
<td>104</td>
</tr>
<tr>
<td>Bi(<em>{0.5})Sr(</em>{0.5})Co(<em>{0.5})Fe(</em>{0.5})O(_{3-\delta})</td>
<td>1173</td>
<td>1.1 \times 10(^{-6})</td>
<td>1.2</td>
<td>0.021</td>
<td>0.00065</td>
<td>3.8 \times 10(^{-8})</td>
<td>105</td>
</tr>
<tr>
<td>La(<em>{0.6})Ca(</em>{0.4})Co(<em>{0.5})Fe(</em>{0.5})O(_{3-\delta})</td>
<td>1173</td>
<td>1.2 \times 10(^{-7})</td>
<td>1.0</td>
<td>0.020</td>
<td>0.00053</td>
<td>3.3 \times 10(^{-9})</td>
<td>106</td>
</tr>
<tr>
<td>In(_2)O(_3)–55 mass % Bi(_2)O(_3)</td>
<td>1073</td>
<td>5.3 \times 10(^{-8})</td>
<td>2.9</td>
<td>0.021</td>
<td>0.0054</td>
<td>1.1 \times 10(^{-9})</td>
<td>79</td>
</tr>
<tr>
<td><strong>Molten oxide materials</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>In(_2)O(_3)–48 mass % Bi(_2)O(_3)</td>
<td>1123</td>
<td>8.7 \times 10(^{-8})</td>
<td>2.6</td>
<td>0.021</td>
<td>0.0038</td>
<td>1.3 \times 10(^{-8})</td>
<td>95</td>
</tr>
<tr>
<td>Co(_3)O(_4)–36 mass % Bi(_2)O(_3)</td>
<td>1123</td>
<td>1.9 \times 10(^{-7})</td>
<td>2.0</td>
<td>0.021</td>
<td>0.0047</td>
<td>2.5 \times 10(^{-8})</td>
<td>17</td>
</tr>
</tbody>
</table>
To compare the performance of different ion transport membrane materials for oxygen separation, one should determine the specific oxygen permeation rate \( j_{\text{O}_2}^* \), or the oxygen permeability

\[
j_{\text{O}_2}^* = j_{\text{O}_2} h = \frac{h}{\ln(P_{\text{O}_2}^*/P_{\text{O}_2})}
\]

This expression was used to calculate the \( j_{\text{O}_2}^* \) values only for those membrane materials that exhibit high rate of surface exchange reactions (Table 2).103 As can be seen, the oxygen permeabilities of the molten oxide LGBS membrane materials and those of the best ceramic membrane materials are comparable.

IV.4. Selectivity

Molten oxide LGBS membrane materials exhibit very high oxygen selectivity.17 A chromatogram in Fig. 19a confirms high oxygen selectivity of the molten oxide LGBS membrane material Co\(_3\)O\(_4\)–36 mass% Bi\(_2\)O\(_3\). According to this chromatogram, the nitrogen flux through the material is almost zero, i.e., \( j_{\text{O}_2}/j_{\text{N}_2} \to \infty \). Assuming that the nitrogen concentration in the permeate flux is beyond the sensitivity limit of the gas chromatograph (10\(^{-5}\) g ml\(^{-1}\)), the oxygen selectivity of the membrane material in question is estimated at \( j_{\text{O}_2}/j_{\text{N}_2} > 10^5 \). So high oxygen selectivity is possible if nitrogen present in air is not dissolved in the molten oxide responsible for the gas tightness of the membrane material.

Thus, the molten oxide LGBS membrane material Co\(_3\)O\(_4\)–36 mass% Bi\(_2\)O\(_3\) exhibits high oxygen selectivity and permeability (see Fig. 19, Table 2) and can therefore be used in separators for producing ultrahigh purity oxygen for micro- and nanoelectronics, biotechnology, pharmaceutical industry and other fields of science and technology.

V. Molten oxide fuel cells

Fuel cells convert chemical energy to electricity with high efficiency and no environmental pollution. Usually, fuel cells are classified with respect to electrolyte. There are two classes of fuel cells, viz., high-temperature and low-temperature (main types of fuel cells are characterized in Table 3).107,108 High-temperature solid-oxide fuel cells have efficiencies of nearly 70% and are therefore of considerable interest for practice. Traditionally, solid-oxide fuel cells operate in the temperature interval of 1073–1273 K. High operating temperature accelerates the degradation of electrolytes and electrode materials used in the fuel cells. To solve the problem, the operating temperature should be reduced to 773–1073 K; however, this is accompanied by a significant decrease in the ionic conductivity of the electrolytes for the solid-oxide fuel cells (YSZ, GDC, etc.) and in the rates of electrode reactions.

In the last decade, much research efforts were aimed to search for novel materials with high oxygen ion conductivity at 773–1073 K.109–114 For instance, Zhu et al.112 proposed a composite electrolyte ‘solid GDC–eutectic melt Li\(_2\)CO\(_3\)–Na\(_2\)CO\(_3\)–K\(_2\)CO\(_3\)’ having high oxygen ion conductivity at 873 K. However, application of this electrolyte in fuel cells is difficult because a mixture of CO\(_2\) and O\(_2\) is required as cathode gas. To solve the problem, a concept of molten oxide fuel cell with air as cathode gas was proposed.113 Here MOE is the molten oxide LGBS electrolyte in fuel cells is difficult because a mixture of CO\(_2\) and O\(_2\) is required as cathode gas. To solve the problem, a concept of molten oxide fuel cell with air as cathode gas was proposed. An air/chromel/MOE/chromel/CO fuel cell was fabricated;113 here MOE is the molten oxide LGBS electrolyte TeO\(_2\)–16 mass% Te\(_2\)Bi\(_2\)O\(_{11}\) consisting of solid TeO\(_2\) grains (dark areas in Fig. 20) and oxygen-ion-conducting intergranular liquid channels (light areas in Fig. 20). Since solid TeO\(_2\) grains do not conduct oxygen ions, the ionic conductivity in the MOE was strongly limited by the content of the liquid phase (recall that from mechanical strength considerations the volume fraction of the liquid phase in the molten oxide material should not exceed 30 vol.% – 35 vol.%).

Recently, a highly conductive molten oxide LGBS electrolyte \( \delta\)-Bi\(_2\)O\(_3\)–0.2 mass% Bi\(_2\)O\(_3\) was developed; here, both solid \( \delta\)-Bi\(_2\)O\(_3\) grains and intergranular liquid channels conduct oxygen ions.16 The conductivity of this composite is plotted vs. temperature in Fig. 21. This dependence exhibits three characteristic temperature intervals, namely, 823–898, 898–1003 and 1003–1053 K. According to the phase diagram of the Bi\(_2\)O\(_3\)–Bi\(_2\)O\(_3\) system,115 the first temperature interval corresponds to the conductivity of ceramic composite \( \alpha\)-Bi\(_2\)O\(_3\)–Bi\(_2\)O\(_3\). The kink at 898 K in the conductivity curve is due to peritectic decomposition of Bi\(_2\)B\(_2\)O\(_9\) and formation of the molten oxide LGBS composite \( \alpha\)-Bi\(_2\)O\(_3\)–0.2 mass% Bi\(_2\)O\(_3\). Therefore, the second temperature interval corresponds to the conductivity of this composite. The conductivity jump at 1003 K is due to the polymorphic transformation \( \alpha\)-Bi\(_2\)O\(_3\)–\( \delta\)-Bi\(_2\)O\(_3\); it is accompanied by abrupt increase in the oxygen ion conductivity.98–100 Thus, the third temperature interval corresponds to the conductivity of the molten oxide LGBS
The oxygen ion transport number of this composite determined by the volumetric measurements of the faradaic efficiency technique\(^{16}\) was 0.96 ± 0.03 at 1023 K. This confirms high oxygen ion conductivity of the composite in the temperature interval of 1003 – 1053 K. The ionic conductivity of the composite is governed by both the solid phase δ-Bi\(_2\)O\(_3\) and the intergranular liquid channels; it cannot be ruled out that the solid δ-Bi\(_2\)O\(_3\)/melt interfaces also contribute to the ionic conductivity.\(^{116, 117}\)

For comparison, Table 4 lists the performance characteristics of different fuel cells including the molten oxide ones. As can be seen, the molten oxide fuel cells are characterized by high current density and low operating voltage, which seems to be due to the low decomposition potential of the oxides Bi\(_2\)O\(_3\) and TeO\(_2\) as components of the molten oxide electrolytes. In the future, it is of interest to study the transport properties of the molten oxide LGBS electrolytes YSZ–Bi\(_2\)O\(_3\) and GDC–Bi\(_2\)O\(_3\) with higher decomposition potentials.

**VI. Modelling. The dynamic polymer chain model**

A key issue to the membrane and electrolyte materials considered in this review concerns the mechanism of oxygen transport through the membranes.

---

**Table 3. Fuel cell types.**\(^{108}\)

<table>
<thead>
<tr>
<th>Fuel cell</th>
<th>T/K</th>
<th>Anode reaction</th>
<th>Cathode reaction</th>
<th>Charge carrier in electrolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFC</td>
<td>&lt;373</td>
<td>H(_2) + 2H(_2)O \rightarrow 2H(_2)O + 2e(^-)</td>
<td>1/2O(_2) + H(_2)O + 2e(^-) \rightarrow 2H(_2)O + H(^+)</td>
<td></td>
</tr>
<tr>
<td>PEMFC</td>
<td>333–393</td>
<td>H(_2) \rightarrow 2H(^+) + 2e(^-)</td>
<td>1/2O(_2) + 2H(^+) + 2e(^-) \rightarrow H(_2)O + H(^+)</td>
<td></td>
</tr>
<tr>
<td>DMFC</td>
<td>333–393</td>
<td>MeOH + H(_2)O \rightarrow CO(_2) + 6H(^+) + 6e(^-)</td>
<td>3/2O(_2) + 6H(^+) + 6e(^-) \rightarrow 3H(_2)O + H(^+)</td>
<td></td>
</tr>
<tr>
<td>PAFC</td>
<td>433–493</td>
<td>H(_2) \rightarrow 2H(^+) + 2e(^-)</td>
<td>1/2O(_2) + 2H(^+) + 2e(^-) \rightarrow H(_2)O + H(^+)</td>
<td></td>
</tr>
<tr>
<td>MCFC</td>
<td>873–1073</td>
<td>H(_2) + CO(_2) \rightarrow H(_2)O + CO(_2) + 2e(^-)</td>
<td>1/2O(_2) + CO(_2) + 2e(^-) \rightarrow CO(^2)-</td>
<td></td>
</tr>
<tr>
<td>SOFC</td>
<td>1073–1273</td>
<td>H(_2) + O(^2)(^-) \rightarrow H(_2)O + 2e(^-)</td>
<td>1/2O(_2) + 2e(^-) \rightarrow O(^2)-</td>
<td></td>
</tr>
</tbody>
</table>

**Note.** Fuel cell (FC) notations are as follows: AFC is Alkaline, PEMFC is Polymer Electrolyte Membrane, DMFC is Direct Methanol, PAFC is Phosphoric Acid, MCFC is Molten Carbonate, SOFC is Solid Oxide.

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The oxygen transport number of this composite determined by the volumetric measurements of the faradaic efficiency technique\(^{16}\) was 0.96 ± 0.03 at 1023 K. This confirms high oxygen ion conductivity of the composite in the temperature interval of 1003 – 1053 K. The ionic conductivity of the composite is governed by both the solid phase δ-Bi\(_2\)O\(_3\) and the intergranular liquid channels; it cannot be ruled out that the solid δ-Bi\(_2\)O\(_3\)/melt interfaces also contribute to the ionic conductivity.\(^{116, 117}\)

For comparison, Table 4 lists the performance characteristics of different fuel cells including the molten oxide ones. As can be seen, the molten oxide fuel cells are characterized by high current density and low operating voltage, which seems to be due to the low decomposition potential of the oxides Bi\(_2\)O\(_3\) and TeO\(_2\) as components of the molten oxide electrolytes. In the future, it is of interest to study the transport properties of the molten oxide LGBS electrolytes YSZ–Bi\(_2\)O\(_3\) and GDC–Bi\(_2\)O\(_3\) with higher decomposition potentials.

**VI. Modelling. The dynamic polymer chain model**

A key issue to the membrane and electrolyte materials considered in this review concerns the mechanism of oxygen transport through the membranes.

---

**Table 4. Performance characteristics of fuel cells.**

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>I/mA cm(^{-2})</th>
<th>U/V</th>
<th>h/mm</th>
<th>T/K</th>
<th>Ref.</th>
</tr>
</thead>
</table>
| Ce\(_0.8\)Sm\(_0.2\)O\(_1.9\) – 20 mass % (Li\(_2\)CO\(_3\) – 33 mol.% Na\(_2\)CO\(_3\)) | 480  
| Ce\(_0.8\)Sm\(_0.2\)O\(_1.9\) – 20 mass % (Li\(_2\)CO\(_3\) – 33 mol.% Na\(_2\)CO\(_3\)) | 500  
| Ce\(_0.8\)Sm\(_0.2\)O\(_1.9\) – 30 mass % (Li\(_2\)CO\(_3\) – 31.5 mol.% Na\(_2\)CO\(_3\) – 25 mol.% K\(_2\)CO\(_3\)) | 1300  
| TeO\(_2\) – 16 mass % Te\(_2\)Bi\(_3\)O\(_11\) | 720  
| δ-Bi\(_2\)O\(_3\) – 0.2 mass % B\(_2\)O\(_3\) | 1550  

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Figure 20. Microstructure (fracture face) of the molten oxide LGBS composite TeO\(_2\)–16 mass % Te\(_2\)Bi\(_3\)O\(_11\) after cooling from 913 K.\(^{15}\)

Figure 21. Conductivities of molten oxide electrolytes (1, 2) and conventional electrolytes (3–5) plotted vs. temperature.\(^{16}\) TeO\(_2\)–16 mass % Bi\(_2\)O\(_3\) (1), δ-Bi\(_2\)O\(_3\)–0.2 mass % B\(_2\)O\(_3\) (2), Ce\(_0.8\)Sm\(_0.2\)O\(_1.9\)–50 vol.% Li\(_0.62\)K\(_0.38\)CO\(_3\) (3), 8YSZ (4) and Ce\(_{0.9}\)Gd\(_{0.1}\)O\(_2\).\(^{14}\) (5).
ion transport in molten oxides. Recently, a number of models for mass transport in molten oxides have been proposed.\textsuperscript{22,121–123} In particular, the dynamic polymer chain model describes the oxygen ion transport in the molten oxides based on V\textsubscript{2}O\textsubscript{5}.\textsuperscript{22} Prior to discussing the model, we will briefly outline the structure of melts.

The structures of molten V\textsubscript{2}O\textsubscript{5} and binary systems based on it were studied by X-ray and neutron diffraction, NMR spectroscopy, Raman spectroscopy, etc.\textsuperscript{124–134} It was established that melting of V\textsubscript{2}O\textsubscript{5} causes the intramolecular coordination of atoms to change insignificantly. Nevertheless, some of weak bonds V–O break and chains of distorted tetrahedra VO\textsubscript{4} or trigonal bipyramids VO\textsubscript{5} are formed, as in the glassy oxides based on V\textsubscript{2}O\textsubscript{5} (Fig. 22). The average number of structural units in the chain depends on the temperature, being equal to 120 at 973 K.\textsuperscript{133}

The structure of oxide glasses based on Bi\textsubscript{2}O\textsubscript{3} was intensively studied by X-ray diffraction, atomic absorption spectroscopy, Raman spectroscopy, IR spectroscopy, electron paramagnetic resonance, etc.\textsuperscript{135–144} It was shown that glassy Bi\textsubscript{2}O\textsubscript{3} forms trigonal pyramids BiO\textsubscript{3} or distorted octahedra BiO\textsubscript{6}. Based on IR spectroscopy data, Milanova \textit{et al.}\textsuperscript{144} proposed that the structure of glassy bismuth oxide can also be built of BiO\textsubscript{n} polyhedra. Taking account of the aforesaid, one can admit the presence of trigonal pyramids BiO\textsubscript{3} or distorted octahedra BiO\textsubscript{6} in the structure of molten Bi\textsubscript{2}O\textsubscript{3}.

Consider the oxygen ion transport in molten V\textsubscript{2}O\textsubscript{5} within the framework of the dynamic polymer chain model. The process is schematically shown in Fig. 23. The key points of the model are as follows:

— the melt has a polymeric structure;
— the average length of the polymer chain is temperature dependent;
— breakdown and connection of polymer chains in the melt occur stochastically and isentropically;
— breakdown of a polymer chain causes the formation of two chains with a terminal oxygen pseudovacancy in one of them;
— chain connection is followed by release of one of two terminal oxygen ions;
— the free oxygen ion is trapped by the nearest pseudovacancy;
— transport of oxygen ions and electrons through the melt is driven by the electrochemical potential gradient;
— the relative migration rates of oxygen anions and electrons are balanced so the total charge transferred is zero.

The oxygen ion transport in molten V\textsubscript{2}O\textsubscript{5} within the framework of this model is schematically shown in Fig. 23. An oxygen ion chemisorbed on the melt surface (stage \textit{I}) is trapped by the nearest terminal pseudovacancy. As a result, a terminal oxygen is formed (stage \textit{II}). The subsequent chain connection results in the formation of a free oxygen ion (stage \textit{III}), which is trapped by the nearest pseudovacancy, \textit{etc}. Eventually, the free oxygen ion arrives at the

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig22.png}
\caption{Structure of V\textsubscript{2}O\textsubscript{5}: melt (a) and crystal (b).
}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig23.png}
\caption{Oxygen ion transport in molten V\textsubscript{2}O\textsubscript{5}: a schematic.\textsuperscript{68} Mobile oxygen (1), terminal oxygen (2), bridging oxygen (3) and oxygen pseudovacancy (4).
}
\end{figure}

The electronic conductivity of the melt is provided by vanadium:

\[ V^{5+} + e^- \rightarrow V^{4+} \]  

(44a)

In accordance with the model, there is one oxygen pseudovacancy per two chains, each containing \( N \) metal atoms and \( xN/2 \) oxygen atoms (\( x \) is the oxidation state of the metal). Thus, the concentration of oxygen pseudovacancies (\( c_i \)) or mobile oxygen ions, is \( xN \) times lower than the concentration of oxygen atoms in the molten oxide (\( c_m \))

\[ c_i = \frac{c_m}{xN} \]

(45)

The concentration of oxygen atoms is given by

\[ c_m = \frac{x\rho}{2M} \]

(46)

where \( \rho \) and \( M \) are the density and molar mass of the molten oxide, respectively. Substituting Eqn (46) into relation (45), one gets the following expression for the concentration of charge carriers:

\[ c_i = \frac{\rho}{xN} \]

(47)

The oxygen ion conductivity in the melt is given by

\[ \sigma_i = B_i \frac{c_i F}{c} \]

(48)

In accordance with the Nernst–Einstein equation,

\[ B_i = \frac{D_i c_i^2 F^2}{RT} \]

(49)

where \( D_i \) is the diffusion coefficient of oxygen ions in the melt. Substituting Eqn (49) into Eqn (48) gives the following expression for the ionic conductivity:

\[ \sigma_i = \frac{D_i c_i^2 F^2}{RT} \]

(50)

Since the liquid phase percolates in the molten oxide membrane materials (see Figs 8, 9, 20), their oxygen ion conductivity (\( \sigma_i \)) can be expressed as follows:

\[ \sigma_i = \eta \sigma_1 \]

(51)

where \( \eta \) is the volume fraction of the liquid phase in the molten oxide membrane material. Using Eqns (38), (47), (50) and (51), one gets the expression for the oxygen flux through the molten oxide membranes:

\[ j_{O_2} = \frac{\rho D_i}{8MN} \ln \left( \frac{P_{O_2}}{P_{O_2}} \right) \]

(52)

Experimental \( j_{O_2} \) values and the results of calculations using formula (52) for the molten oxide membranes based on \( \text{V}_2\text{O}_5 \) (\( N = 120 \)) (Ref. 22) and \( \text{Bi}_2\text{O}_3 \) (\( N = 1 \)) (Ref. 145) are in order-of-magnitude agreement, thus confirming the correctness of the model.

Our analysis of published data revealed some recent advances in the design of novel molten oxide electrochemical materials. Based on the results obtained, these materials may find application in electrochemical devices for power generation and oxygen production for various fields from power engineering to nanoelectronics and biotechnology. However, studies on these materials raised a number of issues that should be clarified. In particular, ideas about the mechanisms of oxygen ion transport in molten oxides are underdeveloped. The mechanical properties of molten oxide materials have been poorly studied so far. This makes the assessment of their potential for technological applications difficult. Specific features of the influence of the solid oxide/liquid oxide interfaces on the transport properties of molten oxide materials are unascertained. The formation of space charge regions with high ionic conductivity near interfaces was reported.\(^{116, 117}\) In this connection, the concept of liquid-channel grain-boundary nanostructure\(^{34}\) offers great prospects for the design of molten oxide nanomaterials with oxygen ion conductivity.

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References

113. C Xia, Y Li, Y Tian, Q Liu, Y Zhao, L Jia, Y Li *J. Power Sources* **188** 156 (2009)
114. C Xia, Y Li, Y Tian, Q Liu, Z Wang, L Jia, Y Zhao, Y Li *J. Power Sources* **195** 3147 (2010)
133. V M Mastikhin, O B Lapina, L G Simonova *Rasplavy* (2) 21 (1990)
134. O A Esin, V P Gel’d *Fizicheskaya Khimiya Ispuskov Keramicheskikh Rasplavov* (Physical Chemistry of Pyrometallurgical Processes) (Moscow: Metallurgiya, 1966)