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# Modification of Functional Properties of Perovskite-Like Oxides with Mixed Conductivity, New Approaches and Their Research Methods

I. V. BELEN'KAYA<sup>1</sup>, M. P. POPOV<sup>1</sup>, I. A. STARKOV<sup>1</sup>, O. A. SAVINSKAYA<sup>1</sup>, S. F. BYCHKOV<sup>1</sup>, and A. P. NEMUDRY<sup>1,2</sup><sup>1</sup>*Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch, Russian Academy of Sciences, Ul. Kutateladze 18, Novosibirsk 630128 (Russia)**E-mail: nemudry@solid.nsc.ru*<sup>2</sup>*Novosibirsk State University, Ul. Pirogova 2, Novosibirsk 630090 (Russia)*

## Abstract

A strategy of targeted regulating functional properties of perovskite-like oxides with mixed oxygen-electronic conductivity (MOEC) using ferroelectric high-valent dopants (Nb, Ta, Mo, and W) is presented. New research methods of the oxygen stoichiometry and oxygen exchange kinetics in MOEC oxides were proposed. Research results of oxygen permeability of membranes based on the elaborated materials were discussed.

**Key words:** nonstoichiometric perovskites, oxygen permeable membranes, oxygen transport mechanism

## INTRODUCTION

Perovskite-like oxides with mixed oxygen-electronic conductivity (MOEC) are promising for their use as oxygen permeable membranes, selective sorbents, electrode materials for solid oxide fuel cells (SOFC), sensors, *etc.* [1, 2]. As a rule, oxygen exchange in MOEC oxides with rates suitable for the practical use can be achieved only at the temperatures above 600 °C. However, in a number of cases, this disadvantage becomes an advantage: for example, oxygen separation from air using oxygen-permeable membranes is built into the high-temperature processes of partial oxidation of hydrocarbons [3, 4], methane dimerization [5, 6], and efficient fuel consumption [7].

For the elaboration of these innovation technologies, MOEC materials with the desired properties are necessary, as well as understanding their functioning mechanism. The major functional property of MOEC materials is the oxygen exchange of oxide with the gas phase that is determined by its oxygen stoichiometry.

This work presents the results of studies carried out over the last 10 years at the Laboratory of Chemical Materials Science of the ISSCM, SB RAS (Novosibirsk) on the target modification of properties of perovskite-like oxides with mixed conductivity by their doping with ferroelectric highly charged cations Nb, Ta(V) and Mo, W(VI), as well as new methods and approaches to research of the oxygen stoichiometry and oxygen exchange mechanism in MOEC oxides.

## STRATEGY OF DOPING MOEC OXIDES WITH FERROELECTRIC HIGHLY CHARGED CATIONS

As a whole, MOEC oxides refer to three structural types: cubic perovskite  $ABO_{3-\delta}$ , perovskite-like oxides with  $K_2NiF_4$  structural type (Ruddlesden – Popper phase) and double perovskites  $A_2BB'O_{6-\delta}$ . Currently, cubic perovskites possess the best transport properties. The variety basis of cubic MOEC perovskite is nonstoichiometric  $SrCoO_{3-\delta}$  (SC) and  $SrFeO_{3-\delta}$  (SF)

perovskites, moreover, cobaltite possesses a higher mixed conductivity, while ferrite is more stable at low partial pressures of oxygen  $p_{O_2}$ . These characteristics are successfully combined in perovskites with the compositions of  $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$  (SCF) and  $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$  (BSCF) that are record holders on oxygen permeability [1, 2].

Prospects of using MOEC perovskites in various technological processes dictate the necessity of the targeted regulation of their functional properties including an increase of stability in atmosphere with low  $p_{O_2}$  and containing  $CO_2$ , suppression of phase (perovskite-brownmillerite, SCF) and polymorphous (cubic-hexagonal perovskite, BSCF) conversions that destruct materials under operation conditions and reduce oxygen flows. Several attempts [8–11] to modify properties of strontium ferrites/cobaltites by partial isomorphous ion substitution in A and B cations sublattices are known. Literature data analysis allows making the following conclusions:

- Substitution of  $Sr^{2+}$  by rare earth  $Ln^{3+}$  increases the stability of MOEC materials but on an order of magnitude decreases oxygen flows.

- Substitution of B cations by metals with a fixed valence, for example,  $B^{3+}$  (Al, Ga, In) and  $B^{4+}$  (Ti, Zr), leads to the range decrease of the oxygen stoichiometry and a more stable behaviour under redox conditions. The crystal lattice expansion at temperature and oxygen partial pressure  $p_{O_2}$  variation decreases, but herewith, oxygen permeability also drops [8–11].

A new strategy on regulating functional properties of MOEC oxides by their doping with ferroelectric highly charged  $B^{5+}$  (Nb, Ta) and  $B^{6+}$  (Mo, W) cations was proposed by us [12–20]. Its basis is the idea of perovskites as of ferroics, *i.e.* of the materials that show ferroelectric properties: ferromagnetism, ferroelectricity and ferroelasticity. According to data of [21] and research carried out by us [22], MOEC oxides are ferroelastics. At a phase transition from a high temperature cubic phase into a low temperature low symmetry, mechanical stresses arise in the material that are minimized by twinning (Fig. 1).

Ferroelectrics and ferroelastics have the united nature, in connection with which one can try to use models and approaches developed for well-studied ferroelectric relaxors to describe MOEC oxides with significant compositional dis-

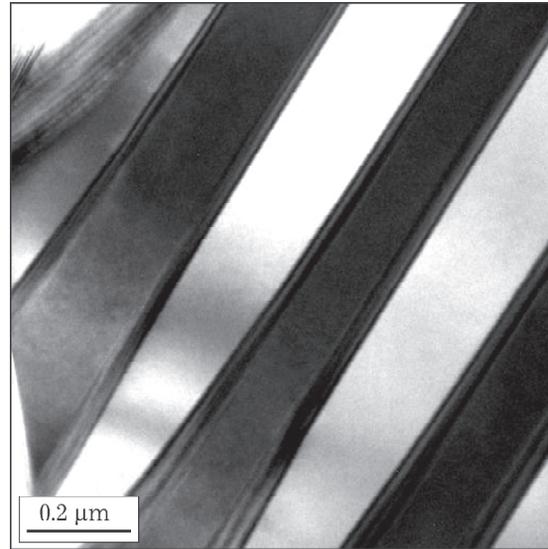


Fig. 1. Data of electron microscopy: bright field image of  $SrCo_{0.8}Fe_{0.2}O_{2.5}$  after a phase transition cubic perovskites–rhomboidal brownmillerite.

order. In particular, according to the approach proposed, in case of a significant deviation from oxygen stoichiometry and/or doping with ferroelectric highly charged  $B^{5+}$  (Nb, Ta) and  $B^{6+}$  (Mo, W) cations of MOEC oxides, a high temperature phase should be in the ergodic state, typical for ferroelectric relaxors. The data on the study of the structure and microstructure of the samples obtained by quenching high temperature state of MOEC oxides that are doped with highly charged cations (Nb, Ta, Mo, and W) are consistent with this suggestion.

The formation of characteristic texture can be seen in microphotographs: nanoscale  $90^\circ$  domains disoriented in six possible  $\langle 100 \rangle_p$  directions (Fig. 2, a) and forming the glassy state with the averaged cubic symmetry (see Fig. 2, b) when increasing the compositional disorder (substitution degree of cobalt ions with highly charged dopants). The glassy state in ferroelectric relaxors is interpreted as a result of quenching dynamic polar nanodomains existing in the ergodic state.

Thus, analogously to ferroelectric relaxors MOES oxides with the compositional disorder can be regarded as ferroelastic relaxors, for which blurring of the phase transition perovskite-brownmillerite and the presence of the ergodic (dynamic nanostructured) state at high temperatures that when cooling transfers into

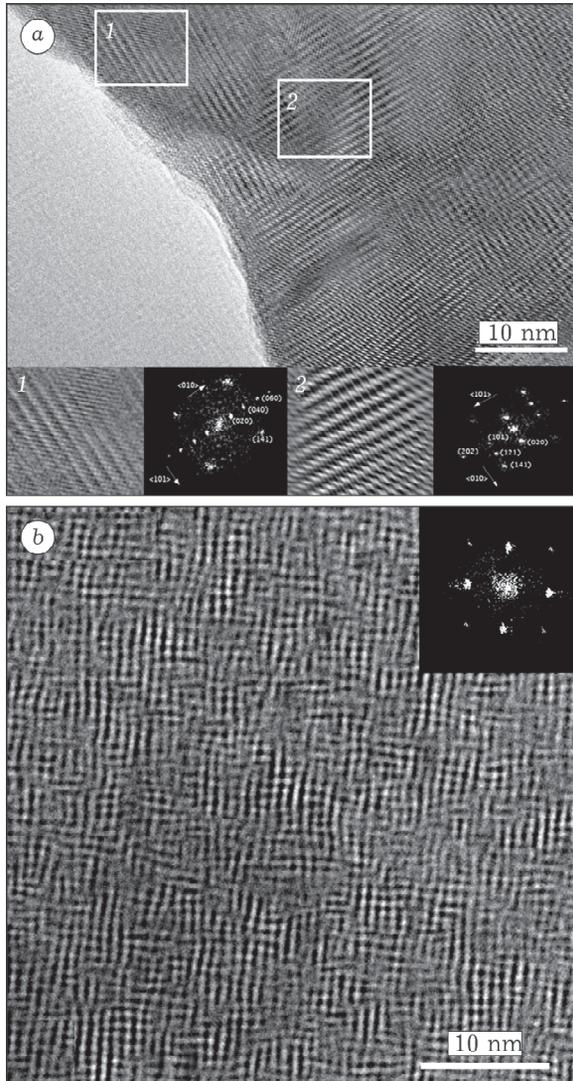


Fig. 2. Data of transmission electron microscopy and appropriate diffraction images obtained by the fast Fourier transform for MOES oxides of the composition of  $\text{SrCo}_{0.73}\text{Fe}_{0.2}\text{Ta}_{0.07}\text{O}_{2.58}$  (a) and  $\text{SrCo}_{0.7}\text{Fe}_{0.2}\text{Ta}_{0.1}\text{O}_{2.6}$  (b).

static nanodomain texture are characteristic. As is known, the phase transition perovskite–brownmillerite characteristic for SCF perovskite falls into the region of operating conditions of MOES materials ( $T \sim 700\text{--}800\text{ }^\circ\text{C}$ ,  $p_{\text{O}_2} \sim 10^{-2}\text{--}10^{-3}$  atm) in oxygen permeable membranes and SOFC electrodes and serves as the main reason of their destruction. Creating the compositional disorder by doping MOES oxides with highly charged ferroelectric Nb/Ta(V) and Mo/W(VI) cations [23] washes away the phase transition perovskite–brownmillerite and thereby contributes to preserving the integrity of the membrane under operating conditions [24].

From the fundamental viewpoint, the approach to MOES oxides as to ferroelastic relaxors opens up possibilities for deeper understanding the nature of their high oxygen mobility. The specifics of lattice dynamics of ferroelectric/ferroelastic relaxors in the ergodic state with dynamically polar nanodomains (see Fig. 2, b) associated with soft vibrational modes and instability of the crystal lattice can explain superior properties of SCF and other MOES oxides [16, 23–25] at high temperatures. At low temperatures, an abnormally high conductivity of ferrites and cobaltites is determined by the availability of microdomain texture (nanostructuring the material) with a high density of domain walls that ensure facilitated diffusion channels for oxygen transport (see Fig. 2, a) [26–31].

Thus, the use of ferroelectric cations (Nb, Ta, Mo, W) at doping membrane and electrode materials from MOES oxides allows solving the whole range of problems of material science:

1. The availability of the ergodic state accompanying by nanostructuring at decreasing the temperature leads to blurring phase transitions with ordering of oxygen vacancies (perovskite–brownmillerite type) and increasing oxygen conductivity/permeability of MOES materials (Fig. 3) (effect of the trap typical for doped materials is eliminated in this case, since dopant ions and defects ( $\text{V}_\text{O}$ ,  $\text{O}_\text{i}$ ) that ensure oxygen transport are shielded by oxide ions of  $\text{MO}_6$  octahedra).

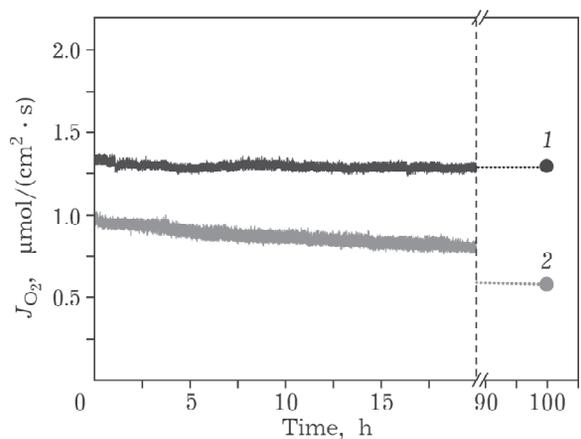


Fig. 3. Dependence of oxygen flows *vs.* time for  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.78}\text{W}_{0.02}\text{Fe}_{0.2}\text{O}_{3-\delta}$  (1) and  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  (2) membranes.  $L = 1.60$  mm.

TABLE 1

Thermal expansion coefficients for  $\text{Sr}_{1-x}\text{La}_x\text{Co}_{0.8-yz}\text{M}_y\text{Fe}_{0.2}\text{O}_{3-\delta}$  and  $\text{SrFe}_{1-x}\text{M}_x\text{O}_{3-\delta}$  perovskites [32],  $10^{-6}/\text{K}$ 

Chemical composition of the material	$297 \leq T, \text{K} \leq 573$	$773 \leq T, \text{K} \leq 1273$
$\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$	21.2	29.3
$\text{SrCo}_{0.5}\text{Fe}_{0.2}\text{Ta}_{0.3}\text{O}_z$	17.6	19.0
$\text{Sr}_{0.7}\text{La}_{0.3}\text{Co}_{0.6}\text{Fe}_{0.2}\text{Nb}_{0.2}\text{O}_z$	16.5	20.3
$\text{SrFeO}_z$	18.2	30.5
$\text{SrFe}_{0.95}\text{Mo}_{0.05}\text{O}_z$	20.0	28.4
$\text{SrFe}_{0.9}\text{Mo}_{0.1}\text{O}_z$	16.1 ( $T < 623 \text{ K}$ )	21.0; 25.9 ( $T > 973 \text{ K}$ )

2. Doping perovskites  $\text{ABO}_{3-\delta}$  by highly charged cations M (M = Nb, Ta, Mo, W) stabilizes charged states of  $\text{B}^{2+}$  (B = Co, Fe)– $\text{W}^{6+}$ ;  $\text{Fe}^{3+}$ – $\text{Mo}^{5+}$ , which increases electron conductivity of materials at low  $p_{\text{O}_2}$  values [25].

3. Stable oxidation degree of highly charged dopants leads to increasing the chemical stability of materials (especially cobalt-containing) at low  $p_{\text{O}_2}$ .

4. High oxidation degree of dopants contributes to lowering ranges of the oxygen stoichiometry and broadening the crystal lattice of materials at varying the temperature and partial pressure of oxygen (Table 1).

5. Acid properties of highly charged cation oxides lower degradation of membrane potentials in a  $\text{CO}_2$  atmosphere.

6. The introduction into the structure of perovskites of highly charged cations M (M = Nb, Ta, Mo, W) that have a trend to the formation of stable double perovskites  $\text{A}_2\text{BMO}_6$  stabilizes the cubic lattice, suppresses polymorphous conversions cubic–hexagonal perovskite.

7. Mo, W oxides serve as catalysts in the reactions of methane conversion into synthesis gas and dimerization with the formation of ethane, which can be used in catalytic membrane reactors (CMR).

#### NEW RESEARCH METHODS OF THE OXYGEN STOICHIOMETRY AND OXYGEN EXCHANGE KINETICS IN MOES OXIDES

##### *Preparation of continuous quasi-equilibrium isotherms $3-\delta-\lg p_{\text{O}_2}$*

The oxygen stoichiometry determines the structure, phase composition and transport properties of MOES oxides. The dependence

of the oxygen stoichiometry on the oxygen partial pressure is used for the determination of the composition and stability boundaries of phases [33], analysis of the defect structure affecting the electron and ion conductivity of materials [34, 35], as well as for calculating thermodynamic data [34]. As a rule, to determine the dependence of the oxygen stoichiometry on the oxygen partial pressure the methods of thermogravimetry (TG) [33, 36] and coulometry [34] are used. In the first case, problems arise when creating gas mixtures with low oxygen partial pressure, in second – a complex hermetic cell based on ittria-stabilized zirconia (YSZ) that combines the properties of an oxygen pump and sensor is necessary. The methods of neutron diffraction [37] and temperature-programmed desorption of oxygen using Oxylyt System (Sensolech Ltd., Germany) YSZ sensors are also used [38, 39]. All the methods listed require large time expenses to obtain points on the equilibrium dependence of the oxygen stoichiometry on discrete values of oxygen partial pressure and expensive equipment.

A setup and new preparation method of *continuous* quasi-equilibrium diagrams  $3-\delta-\lg p_{\text{O}_2}$  in the isothermal mode were developed by us [40, 41].

The method is based on registering the oxygen partial pressure ( $p_{\text{O}_2}$ ) on the output of the flow reactor at stepped changing  $p_{\text{O}_2}$  in a gas carrier. We proposed a mathematical model that takes into account that in the signal registered by the YSZ sensor in the output of the reactor oxygen not only isolating from oxide but initially filled the reactor, as well as delivered to the reactor as water ingress and trace amounts in the inert gas carrier makes a contribution. According to the model, the dependence of

oxygen nonstoichiometry on oxygen partial pressure is described by the following expression:

$$\delta(t) = \delta(0) + \frac{2}{W} \left\{ J_{\text{in}} \int_0^t \frac{p_{\text{O}_2}(t) - p_{\text{O}_2}^{\text{in}}(t)}{p - p_{\text{O}_2}(t)} dt - \frac{V_r p}{RT} \times \right. \\ \left. \times \ln \frac{p - p_{\text{O}_2}(t)}{p - p_{\text{O}_2}(0)} \right\} \quad (1)$$

where  $J_{\text{in}}$  is molar rate of incoming/effluent gas flow, mol/s;  $W$  is number of oxide moles in the reactor;  $p$  is absolute pressure of the gas (1 atm);  $V_r$  is free volume of the reactor, L.

The equation is applicable both for equilibrium and nonequilibrium oxygen release from oxide and allows calculating continuous changing oxygen stoichiometry by measuring  $p_{\text{O}_2}$  on the output of the reactor.

To determine the quasi-equilibrium mode of oxygen release a mathematical criterion was proposed by us: experimental curves  $p_{\text{O}_2} - t$  should permit affine transform at timing on the rate of helium consumption  $F_{\text{He}}$  (in mL/min):  $t^* \propto t F_{\text{He}}$  (2)

To obtain equilibrium data for phase diagrams one should use samples of MOES oxides with a high surface (powdery) and low gas carrier flow rates. By measuring the value of quasi-equilibrium  $p_{\text{O}_2}$  above the sample and knowing the initial stoichiometry of the sample one can determine the continuous dependence  $3 - \delta - \lg p_{\text{O}_2}$  at a given temperature. Based on measurements performed at various temperatures, detailed equilibrium phase diagrams  $3 - \delta - \lg p_{\text{O}_2} - T$  for oxides  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  (Fig. 4),  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  [42] and  $\text{SrFeO}_{3-\delta}$  [41] were determined. The absolute oxygen content at room temperature was determined by iodometric titration. Starting points at various temperatures for binding the calculated relative dependencies  $3 - \delta$  on  $p_{\text{O}_2}$  to absolute values were determined using TG at specified values of  $p_{\text{O}_2}$ .

Thus, using the new method developed detailed phase equilibrium diagrams  $3 - \delta - \lg p_{\text{O}_2} - T$  for  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ ,  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  and  $\text{SrFeO}_{3-\delta}$  oxides were determined. This allowed deeper understanding the nature of the phase the perovskite-to-brownmillerite transformation. It is commonly believed that BM-P transformation in  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  and  $\text{SrFeO}_{3-\delta}$  oxides is a phase transition of order-disorder type and

is conditioned by disordering oxygen vacancies in compounds with  $3 - \delta = 2.5$  at an increase of temperature. It was shown by us that disordering vacancies was a result of a morphotropic transition, adsorption by brownmillerite ( $3 - \delta = 2.5$ ) of oxygen from the gas phase and the formation of disordered perovskite  $P_1$  ( $3 - \delta = 2.5 + x$ ). Additionally, earlier unknown phase transitions  $P_1$ - $P_2$  were detected for the first time for cobalt-containing perovskites.

### Oxygen partial pressure relaxation

The key factor that determines major functional properties of MOES materials is the oxygen exchange of oxides with the gas phase. Not many methods for the study of the mechanism of this process are known. Most common from them is relaxation of conduction electrons (RCE). Additionally,  $\text{O}^{16}/\text{O}^{18}$  isotope exchange (IE) that is the most expensive method, as well as thermogravimetry (TG), are applied. The conduction electrons in the RCE method is not directly connected with the stoichiometry and occurs under the conditions with uncontrolled  $p_{\text{O}_2}$  (due to the release or absorption of oxygen by the sample). This method is limited by the values of  $p_{\text{O}_2} < 10^{-2}$  atm. IE method, in addition to the fact that it is complex and expensive, is not directly associated with

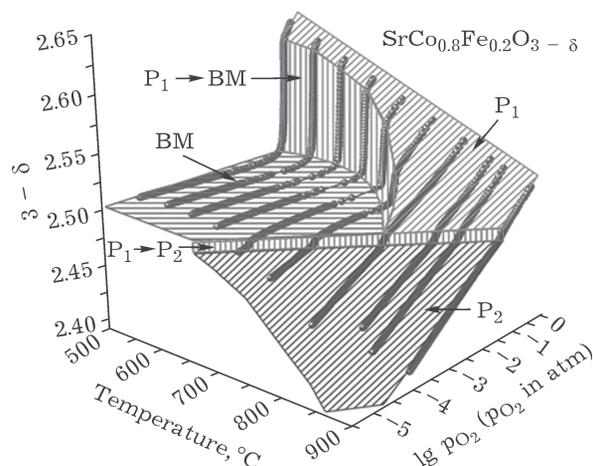


Fig. 4. 3D visualisation of diagrams  $3 - \delta - \lg p_{\text{O}_2} - T$  for  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  perovskite.

nonequilibrium processes [43]. Thermogravimetry is a direct method but due to a large reaction volume, it is virtually impossible to arrange a fast atmosphere replacement for carrying out relaxation measurements.

A new relaxation method, in which  $p_{\text{O}_2}$  serves as a measurable parameter and which is devoid of the above disadvantages, was proposed by us. To carry out relaxation measurements an experimental unit for the study of the processes of oxygen release additionally equipped with a bypass line was used, which allowed decreasing the time constant of the unit up to  $\tau \sim 1$  s. To implement nonequilibrium conditions of oxygen release sintered cylindrical samples of oxides (with the purpose of decreasing the ratio of surface/volume), as well as high carrier gas flow rate (200 mL/min) were used. To obtain the relaxation curve the sample was aged under certain conditions ( $p_{\text{O}_2}^i, T$ ), then the intake partial pressure was stepwise changed up the value of  $p_{\text{O}_2}^f$  and the dependencies  $p_{\text{O}_2} - t$  were registered. The data analysis demonstrated that the dependence of the relaxation rate on time is described well by the falling exponent; therefore, the effective rate constant of oxygen exchange ( $k$ ) can be interpreted as a value inversely proportional to the characteristic relaxation time.

#### *Iso-stoichiometric approach to the study of the oxygen exchange kinetics in strongly nonstoichiometric MOES oxides*

Nonstoichiometric perovskites with the mixed conductivity, as a rule, have very broad homogeneity regions (so called strongly nonstoichiometric compounds), therefore, transport properties of oxides may depend on their composition. Herewith, kinetic parameters of the processes of the oxygen exchange of a strongly nonstoichiometric oxide with the gas phase may vary in the course of kinetic measurements, however, researchers, as a rule, do not take into account stoichiometric changes at a change of temperature or  $p_{\text{O}_2}$ . A suggestion was made by us that kinetic studies (determination of temperature dependences) for strongly nonstoichiometric oxides should be carried out at  $p_{\text{O}_2}$  that

ensures fixed stoichiometry changes of the oxide nonstoichiometry ( $\Delta\delta = \text{const}$ ), relative to the original value. The term iso-stoichiometric was introduced by us for such measurements. Since the release or addition of oxygen is accompanied by the oxygen nonstoichiometry change of oxides, then when carrying out research one should narrow range changing ( $\Delta\delta$ ) and fix initial ( $\delta^i$ ) and final ( $\delta^f$ ) values of stoichiometry by selecting appropriate conditions ( $p_{\text{O}_2}, T$ ).

Nonstoichiometric SCF perovskite was selected as a model object to demonstrate the efficiency of this approach. The homogeneity region of perovskite  $P_1$  was selected for iso-stoichiometric relaxation measurements. Based on the phase diagrams determined earlier  $p_{\text{O}_2}$  values necessary for creating fixed values of  $\delta$  at various temperatures were determined for oxides. The step by  $\delta$  for various samples amounted to 0.01 and 0.005.

Experimental data obtained in the iso-stoichiometric mode, as Arrhenius dependencies for a cylindrical SCF sample ( $h = 6.6$  mm;  $d = 5.43$  mm;  $m = 0.694$  g) are presented in Fig. 5. As seen, the effective activation energy of the oxygen exchange depends on the content of oxygen and increases at a decrease of the oxygen stoichiometry. A change of the activation energy correlates with variations of oxygen partial enthalpy in SCF oxide  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  [33]. Based on this correlation and the value of activation barriers (100–230 kJ/mol) one can claim that the limiting step is the reactions that occur on the oxide surface. Note that with decreasing the oxygen content in oxides at a fixed temperature, the oxygen exchange rate is also decreased.

The dependence of the effective exchange rate constant ( $k$ ) on nonstoichiometry in this case can be presented as

$$k = k^* \exp(-\alpha\delta) = k_0 \exp(-E_0/RT) \exp(-\alpha\delta) \quad (3)$$

where parameter  $\alpha$  (in  $1/\delta$ ) depends on temperature. This dependence has the form:

$$\alpha = \alpha_0 + \alpha_1/RT \quad (4)$$

The application of the equation (4) is limited by nonstoichiometry values used in experiments. Numerical values of  $\alpha_0$  and  $\alpha_1$  parameters were assessed for all SCF cylinders studied:

$$\alpha = -171 \pm 151(1/\delta) + \frac{2012+137}{RT} (\text{kJ}/(\delta \cdot \text{mol})) \quad (5)$$

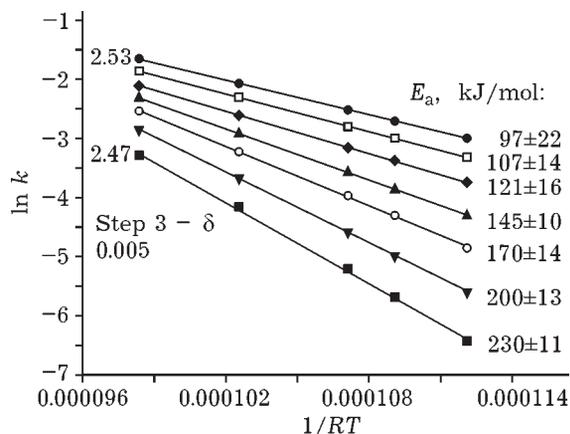


Fig. 5. Arrhenius dependencies for cylindrical sample  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ .

Taking into account the dependence of temperature on  $k$  the equation (3) can be presented as

$$k = k_0 \exp(-\alpha_0 \delta) \exp\left(-\frac{E_0 + \alpha_1 \delta}{RT}\right) \quad (6)$$

The dependence of the effective activation energy on the oxide stoichiometry in the linear approximation yields the value for  $\alpha_1$  that is consistent with the value determined earlier:

$$E_a = -848 \pm 65 \text{ (kJ/mol)} + \delta(2013 \pm 130) \text{ (}\delta \cdot \text{kJ}/(\delta \cdot \text{mol}) \text{)} \quad (7)$$

From the equations (3)–(7), it follows that a decrease of the content of oxygen in oxides, on the one hand, lowers the oxygen exchange rate constant due to an increase of the activation energy ( $\alpha_1 > 0$ ), on the other hand, increases the exchange rate due to an increase of the pre-exponential factor ( $\alpha_0 < 0$ ). This phenomenon is known as the *kinetic compensation effect* (KCE).

#### STUDY OF OXYGEN PERMEABILITY OF DISK MEMBRANES

The process of oxygen permeability through a gastight membrane includes the stages of oxide ions diffusion and release of molecular oxygen from the side of a low partial pressure  $p_{\text{O}_2(2)}$ , therefore, it is interesting to apply the iso-stoichiometric approach to the data analysis on oxygen conductivity of SCF membranes.

To study the process of oxygen permeability of disk ceramic gas tight oxide membranes with a thickness of 1.49–2.2 mm a quartz membrane reactor was used. According to phase

equilibrium diagrams  $3 - \delta - \lg p_{\text{O}_2} - T$  obtained earlier for  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  perovskite, membranes under experimental conditions are in the stability region of the perovskite phase  $P_1$ .

The study of oxygen permeability of SCF membranes demonstrated the dependence absence of oxygen flows  $j_{\text{O}_2}$  on a thickness of membranes ( $1.49 < h < 2.20$ ), which testifies controlling oxygen transport by surface reactions. The oxygen flows obtained have a degree dependence on oxygen partial pressures:

$$j_{\text{O}_2} = \gamma(p_{\text{O}_2(1)}^n - p_{\text{O}_2(2)}^n) \quad (8)$$

The degree  $n$  for all the membranes studied is decreased from 0.6 to 0.4 with temperature increasing from 741 to 934 °C.

It is noteworthy that in oxygen releases from SCF samples in relaxation measurements, the relaxation rate can be described as and the degree function  $p_{\text{O}_2}$  with the changing degree exponent ( $n$ ). Changing the degree exponent ( $n$ ) when varying temperature can be associated with changing nonstoichiometry and accordingly, energetic parameters of nonstoichiometric oxides at an increase in temperature. According to the phase diagram for SCF (see Fig. 4), the dependence of the oxygen nonstoichiometry on  $p_{\text{O}_2}$  in the region of cubic perovskite  $P_1$  phase is close to logarithmic:

$$\delta = \delta_0 - \beta \ln(p_{\text{O}_2}/p_0) \quad (9)$$

Therefore, based on the equation (8), the relaxation rate can be presented as

$$k = k_0 \exp\{(-\alpha_0 - \alpha_1/RT)\delta\} = k_0^* (p_{\text{O}_2}/p)^{\alpha\beta} \quad (10)$$

herewith, the degree exponent is  $n = \alpha\beta$ . A parameter  $\beta$  can be calculated from the phase diagram (see Fig. 4), and a parameter  $\alpha$  – from relaxation data. Degree exponents ( $n$ ) calculated from  $\alpha$  and  $\beta$  parameters and determined from experiments on relaxation and oxygen permeability depending on temperature coincide within the experimental error.

The Arrhenius dependence  $\gamma$  (expression (8)) is not linear and is consistent with literature data. The inclination change, as a rule, is associated with the transition BM–P at disordering oxygen vacancies or with a change of the oxygen permeability mechanism.

However, it was shown by us that operating conditions of the membrane are not beyond the stability region of perovskite phase  $P_1$ . Thus, the non-Arrhenius dependence can be associated

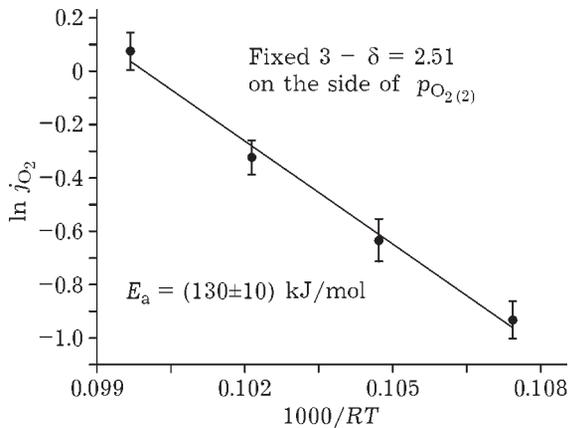


Fig. 6. Arrhenius dependencies of oxygen flows under iso-stoichiometric conditions.

with the effect of the oxygen nonstoichiometry on energetic parameters of the process.

When constructing the dependencies of oxygen flows on a reverse temperature under iso-stoichiometric conditions ( $3 - \delta = 2.51$  on the side of low pressure  $p_{O_2(2)}$ ) (Fig. 6), it can be seen that the dependence is of a linear character, and values of the calculated activation energy amount to  $(130 \pm 15)$  kJ/mol.

#### ELABORATION OF TUBULAR MEMBRANE REACTORS

A preparation technique of tubular membranes by the phase inversion method was perfected by us. Research results of oxygen conductivity with the composition of

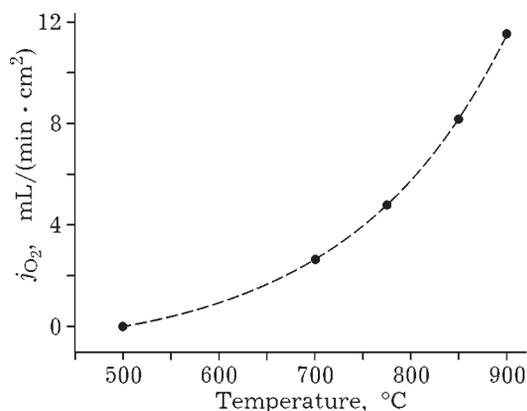


Fig. 7. Dependence of oxygen flows vs. temperature through tubular membranes with the composition of  $Ba_{0.5}Sr_{0.5}Co_{0.78}W_{0.02}Fe_{0.2}O_{3-\delta}$

$Ba_{0.5}Sr_{0.5}Co_{0.78}W_{0.02}Fe_{0.2}O_{3-\delta}$  are presented in Fig. 7. The value of oxygen flows already at  $T > 720$  °C exceeds the level necessary for the economically sound preparation technology of synthesis gas by methane partial oxidation. During testing for 200 h of continuous operation, membranes showed resistance to thermocycling and thermal stresses, as well as stability in the atmosphere containing methane and carbon dioxide.

Thus, the tubular membranes obtained possess high oxygen permeability and stability under the conditions modelling the operation of catalytic membrane reactors.

#### CONCLUSIONS

The research carried out during the last ten years at the Laboratory of Chemical Materials Science of the Institute of Solid State Chemistry and Materials Science (ISSCM), SB RAS allowed obtaining nanoconstructed membrane materials that demonstrate the sustainable operation in long-term tests under conditions corresponding to operation conditions of catalytic membrane reactors (low partial oxygen pressures, atmosphere containing carbon dioxide). Herewith, new materials possess high oxygen permeability and conductivity, which makes them promising for the use in CMR and SOFC.

In order to broaden research methods of oxides with mixed oxygen-electronic conductivity an experimental unit with a flow reactor for carrying out measurements of oxygen release from oxides that possesses a high precision and data collection speed; a mathematical model of oxygen release in a flow reactor for calculating the oxygen nonstoichiometry as a continuous function on oxygen partial pressure was proposed; mathematical criteria of the history (quasi-equilibrium and nonequilibrium) of the process of oxygen release from MOES oxides.

On the ground of research carried out, a determination method of detailed equilibrium diagrams  $3 - \delta - \log p_{O_2} - T$  for MOES based on determining the oxygen nonstoichiometry as a continuous function from oxygen partial pressure was developed. The new method has a number of advantages:

1) allows obtaining data on the oxygen nonstoichiometry as a continuous function from  $p_{O_2}$

(unlike discrete data, obtained in the methods of thermogravimetry and coulometry);

2) relatively simple equipment and a high data collection speed;

3) using a YSZ oxygen sensor ensures a high sensitivity of the method and broadens the measurement range.

For the first time based on continuous dependencies of the oxygen stoichiometry on  $p_{O_2}$ , detailed phase diagrams  $3 - \delta - \lg p_{O_2} - T$  for SCF, BSCF and SF perovskites were obtained. Due to this, one managed to reveal phase transitions, earlier unknown in the literature and show that the high-temperature phase transition brownmillerite–perovskite is morphotropic, *i. e.* vacancies disordering occurs because of adsorption by brownmillerite ( $3 - \delta = 2.5$ ) of oxygen from the gas phase and formation of disordered perovskite  $P_1$  ( $3 - \delta = 2.5 + x$ ).

A new relaxation research method of the oxygen exchange in MOES oxides, in which a precisely measurable parameter is  $p_{O_2}$  was elaborated by us. This allows broadening the measurement range and obtaining data under controllable conditions.

It was shown that for strongly nonstoichiometric perovskites with a mixed conductivity at variation of the oxygen nonstoichiometry, not only structural but also energetic parameters are changed in broad limits, and this affects functional properties of these virtually important oxides. For the correct analysis of properties associated with the oxygen exchange, the formation of reliable conceptions of oxygen transport mechanism one needs to compare kinetic data at the controlled (fixed) stoichiometry, *i. e.* under iso-stoichiometric conditions. When using the traditional isobaric approach ( $\Delta p_{O_2} = \text{const}$ ) non-Arrhenius dependencies and conservative values of the activation energy can be obtained, since changing temperature is simultaneously accompanied by changing the oxide nonstoichiometry.

Using the new method of oxygen partial pressure relaxation and iso-stoichiometric approach it was detected that the activation energy of the process of oxygen release from SCF perovskite was a function of the oxygen stoichiometry of the oxide; decreasing the oxygen content leads to increasing energetic barriers and self-rejection of the reaction of oxygen release.

The results obtained in relaxation experiments were used when analyzing measurements of oxygen permeability for SCF membranes of  $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ . It was shown that the limiting step in oxygen exchange processes between the membrane and gas phase, as and in case of oxygen release from oxides in relaxation experiments were reactions occurring on the membrane surface. An oxygen flow through the membrane increases proportionally to the difference of partial pressures to the power of  $n$ , where  $n$  depends on temperature. Consequently, non-Arrhenius dependence of oxygen flows through an SCF membrane can be associated with decreasing the oxide stoichiometry when increasing temperature, which leads to increasing energetic barriers.

A preparation technique of tubular membranes by the phase inversion method was perfected, data on oxygen permeability, stability of membranes to thermocycling and under the conditions modelling the operation of CMR. Works on creating a membrane module that has the scaling potential for oxygen separation from air and hydrocarbon conversion were started.

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