Transport and Electrochemical Properties of SrFe(Al,Mo)O_{3- δ^1}

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Abstract—In this work, effects of molybdenum doping on the crystal structure, stability, electrical conductivity, oxygen permeability and thermomechanical properties of $Sr(Fe,AI)O_{3-\delta}$ -based perovskites, were studied. The electrochemical performance of model anodes of solid oxide fuel cells (SOFCs), made of $SrFe_{0.7}Mo_{0.3}O_{3-\delta}$, was assessed. Whilst the introduction of Mo cations improves structural stability with respect to the oxygen vacancy ordering processes, excessive molybdenum content leads to a worse phase and mechanical stability under oxidizing conditions. Mo-doping was shown to decrease the thermal and chemical expansivity, to reduce *p*-type electronic conductivity and to increase *n*-type electronic conduction. The oxygen permeation fluxes through gas-tight $Sr_{0.97}Fe_{0.75}Al_{0.2}Mo_{0.05}O_{3-\delta}$ membranes are determined by both the bulk oxygen diffusion and surface exchange kinetics. The role of the latter factor increases on decreasing temperature and reducing oxygen partial pressure. Due to a relatively high electrical conductivity and moderate thermal expansion coefficients in reducing conditions, $SrFe_{0.7}Mo_{0.3}O_{3-\delta}$ -based anodes show a substantially high electrochemical activity.

Keywords: perovskite, strontium ferrite, Mössbauer spectroscopy, thermal expansion, chemical expansion, electronic conductivity, ionic conductivity, solid oxide fuel cell electrodes

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INTRODUCTION

Strontium-ferrite (SrFeO_{3- δ})-based perovskitelike phases with mixed oxygen-ionic and electron conductivity attracted attention as materials for solid oxide fuel cell anodes, as well as membranes for gas separating and hydrocarbon partial oxidation [1-3]. However, serious limitation in the material applications is its high thermal expansion coefficient (TEC) that results in thermomechanical incompatibility of the electrode layers with the solid-electrolyte ceramics. For example, the $Sr_{0.7}La_{0.3}FeO_{3-\delta}$ TEC is 25.6 × 10⁻⁶ K⁻¹ over the 303–1273 K temperature range in air [2]. Another disadvantage of $SrFeO_{3-\delta}$ and its derivatives is their tendency toward the ordering of oxygen vacancies in the case of their high concentration in the perovskite-type crystal lattice. In particular, extensive generation of FeO₄ tetrahedra can lead to the formation of brownmillerite phase that has worse transport properties [1, 4-6].

The iron partial replacement with cations of constant or higher oxidation state allows decreasing the oxygen nonstoichiometry changes and suppressing phase transitions occurring during thermal and redox cycling [3, 6–9]. For example, moderate $SrFeO_{3-\delta}$ doping with aluminum decreased average TEC significantly, the ionic conductivity remaining relatively high. However, the doping cannot entirely prevent the ordered-structure domain formation because of the Al^{3+} cation tendency to be surrounded tetrahedrally with oxygen ions [10]. In addition, localization of electronic charge carriers is impeded at the aluminum cations, resulting in lower electronic conductivity of $\text{SrFe}_{1-x}\text{Al}_x\text{O}_{3-\delta}$ [4, 10]. The introducing of Mo⁶⁺ cations which are partly reduced with the decreasing of oxygen partial pressure is expected to increase the number of the electronic charge carriers, hence, the contribution of *n*-type conductivity under reductive conditions [11-13]. In addition, the loss of the lattice oxygen during the Mo-substituted ferrites reduction is

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515

lower compared to that of $\text{SrFeO}_{3-\delta}$ [13, 14]; ensuring lower chemical expansion. The molybdenum cations are stable in the tetrahedral environment [15–17], which is advantageous for electron and ion transfer; while Mo-containing oxide phases are characterized by high catalytic and electrochemical activity [18, 19]. This approach is significantly limited by possible segregation, under oxidative conditions, of the low-conductive Mo-containing phases, such as AMoO₄ (A = Ca, Sr, Ba) [20–23].

Co-doping with aluminum and molybdenum can allow suppressing the ordering, lowering TEC, and stabilizing the phase with respect to the reductive decomposition. At that, its sufficiently high electron and ionic conductivity is retained under the operation conditions of the solid oxide fuel cell anodes. In this work the effect of molybdenum insertion to $Sr_{1-y}(Fe,AI)O_{3-\delta}$ on the physico-chemical and thermomechanical properties of the materials is studied. Electrochemical characteristics of model anodes of the solid oxide fuel cells are evaluated.

EXPERIMENTAL

The electrode materials, $SrFe_{1-x}Mo_xO_{3-\delta}$ (x = 0.2, 0.3) and $\operatorname{Sr}_{0.97}\operatorname{Fe}_{0.8-x}\operatorname{Al}_{0.2}\operatorname{Mo}_{x}\operatorname{O}_{3-\delta}(x=0.05, 0.1),$ were synthesized by glycine-nitrate method. Aliquots of raw materials, $Sr(NO_3)_2$, $Fe(NO_3)_3 \cdot 9H_2O$, Al(NO₃)₃ \cdot 9H₂O, and (NH₄)₆Mo₇O₂₄ \cdot 4H₂O were dissolved in water, then the solution was added with glycine at one-and-a-half the stoichiometric amount. A powder remained after water evaporation and the mixture spontaneous ignition was repeatedly annealed at 1073-1473 K, to remove organic residues and achieve the components entire interaction. Between the treatments, the powder was re-milled in a planetary ball mill with zirconia balls. To prepare dense ceramic samples, uniaxial pressing was used (at a pressure of 80–100 MPa) of the powders to discs (20 mm in diameter, 0.6-1.5 mm-thick). The ceramics sintering was carried out in air over a 1573–1673 K temperature range. Because the Mo-enriched materials are prone to produce SrMoO₄ under oxidative conditions, the SrFe_{0.7}Mo_{0.3}O_{3- δ} ceramics final sintering was carried out in argon at 1573 K. To investigate stability of the materials under reductive or oxidative conditions, the powders were annealed in a 10% H₂-N₂-H₂O mixture or dry air. The oxygen partial pressure was controlled with a stabilized-zirconia-based sensor.

The materials' phase composition was studied by X-ray diffraction analysis using a Rigaku D/Max-B diffractometer (Rigaku, Japan) with Cu K_{α} radiation ($\lambda = 0.154178$ nm) over the $2\theta = 10^{\circ}-80^{\circ}$ range. The unit cell parameters for single-phase compositions or components of multiphase systems were calculated using Fullprof or PowderCell programs. Mössbauer spectra were obtained at 4.2 K (at samples dipped into liquid He) and 295 K, with the using of standard spec-

trometer with a radiation source 25 mCi ⁵⁷Co in a Rh matrix, under constant acceleration regime. The spectrometer was calibrated using an α -Fe-foil spectrum. Isomer shifts (IS) are given with respect to α -Fe at 295 K. The experimental procedure is described in detail in our previous publications [4, 10, 24–29].

Dilatometric measurements were carried out with parallelepiped ceramic samples using a Linseis L75/N1 vertical dilatometer (Germany). To estimate TEC, the measurements were carried out under continuous heating up to 1373 K and subsequent cooling at a rate of 3 K/min. The chemical expansion was measured with the decreasing of temperature over a 973–1223 K temperature range at a step of 50 K under constant oxygen partial pressure that was controlled in the outlet gas using an electrochemical sensor. The procedure of the measuring of the materials thermomechanical properties is described at length in [7, 30, 31].

The electric conductivity was measured by the four-probe method at constant current in air or gas mixture at a controlled $p(O_2)$; in the latter case case a laboratory set-up described earlier [32] was used. The oxygen permeability across gas-tight ceramic membranes was measured with 1.00- and 1.40-mm-thick samples, using a procedure described in [30, 31]. In the estimating of the ionic conductivity and the surface-exchange kinetic constants, a model [31] was applied, which assumes proportionality between the rate of surface processes and the oxygen chemical potential drop between the gas phase and the membrane surface.

The polarization measurements were conducted in a three-electrode cell in galvanostatic mode using an Autolab 302 NPGSTAT potentiostat/galvanostat (Metrohm Autolab, Netherlands), as described in [30]. A $(La_{0.9}Sr_{0.1})_{0.98}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ membrane (1.5-mmthick, 20 mm in diameter) was used as solid electrolyte; a protective sublayer based on $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ was pre-deposited thereon, in compliance with the recommendations of [30, 33]. A SrFe_{0.7}Mo_{0.3}O_{3 - δ -} based working electrode was deposited onto the sublayer, and then fired-in at 1473 K in argon. A platinum paste was used for the counter-electrode and reference electrode preparation, which was annealed, after its deposition, at a temperature of 1073 K in air. Platinum mesh was used as current collector for the working electrode and counter electrode. Oxygen partial pressure in the anodic compartment was controlled with an oxygen sensor. To evaluate the anode redox-stability, after initial measurements at a constant current density of 100 mA/cm² in a 10% H₂-N₂-H₂O flow, argon was substituted for the gas mixture and the cell was kept under open-circuit conditions for 20 h. Afterwards, the anode compartment was re-filled with the 10% H₂-N₂-H₂O gas mixture, and the measurements were resumed under galvanostatic regime.



Fig. 1. X-ray diffraction patterns of $SrFe_{0.8}Mo_{0.2}O_{3-\delta}$ (a, b) and $SrFe_{0.7}Mo_{0.3}O_{3-\delta}$ (c, d, e) after annealing in air (a, e), in argon (c), in 10% $H_2-N_2-H_2O$ atmosphere (b, d).

RESULTS AND DISCUSSION

 $SrFe_{0.8}Mo_{0.2}O_{3-\delta}$, after the synthesis in air and subsequent annealing under reductive conditions was shown being single-phase and has cubic structure of perovskite (Figs. 1a and 1b, Table 1). After the synthesis in argon, $SrFe_{0.7}Mo_{0.3}O_{3-\delta}$ crystallizes in mono-

clinic syngony $P2_1/m$ (Fig. 1c). Reduction of the material in 10% H₂-N₂-H₂O-atmosphere does not change its phase structure (Fig. 1d); however, in air a layered impurity phase $Sr_3(Fe,Mo)_2O_{7-\delta}$ forms (Fig. 1e). Further owing to its partial decomposition further studies of $SrFe_{0.7}Mo_{0.3}O_{3-\delta}$, were carried out in reductive or inert atmosphere. To elucidate structure changes occurring in $SrFe_{1-x}Mo_xO_{3-\delta}$ during its transition from the x = 0.2 composition to the x = 0.3 one, the materials were studied using Mössbauer spectroscopy; the results obtained will be disclosed below. The presence of cationic vacancies in Sr_{0.97}Fe_{0.8 - x}Al_{0.2}Mo_xO_{3 - δ} results in formation of $Sr_8(Al_{12}O_{24})(MoO_4)_2$ minor (1-3%) impurity (Fig. 2). In reductive atmosphere, $Sr_3Al_2O_6$ formation is also possible, with predominant retention of the perovskite phase (Fig. 2c). On the whole, the substituting of molybdenum for iron results in increase of the unit cell volume (Table 1), owing to the increase in Fe³⁺ concentration, which is also confirmed by the Mössbauer spectroscopy results.

Mössbauer spectra of a $SrFe_{0.8}Mo_{0.2}O_{3-\delta}$ sample quenched in air from 1223 K are presented in Figs. 3a and 4a. Because two peaks are clearly observed in the region from +2.4 to +3.3 mm/s, the SrFe_{0.8}Mo_{0.2}O_{3- δ} spectrum at 4 K was analyzed with three distributions of hyperfine magnetic fields (B_{hf}) , as discussed in [24]. Averaged spectral parameters (Table 2) are characteristic of Fe³⁺, Fe⁴⁺, and Fe⁵⁺ in perovskites. Cations Fe^{4+} coexisting with Fe^{5+} and Fe^{3+} at 4 K exist in socalled localized state that manifests itself also in some perovskite-like ferrites, e.g., $Ln_{0.5}A_{0.5}FeO_{3-\delta}$ (Ln = La, Pr, Nd; A = Sr, Ba), $La_{1-y}Sr_yFe_{1-x}Al_xO_{3-\delta}$, $La_{0.33}Sr_{0.67}Fe_{1 - x}Co_{x}O_{3 - \delta}$, $SrFe_{1 - x}Ti_{x}O_{3 - \delta}$, and $Sr_{3}Fe_{1,9}Mo_{0,1}O_{7\pm\delta}$ [24–26, 34, 35]. Their availability becomes apparent also at 295 K, their IS being lower than for Fe⁴⁺ ions in delocalized electron state, which disproportionate at the lowering of temperature into Fe³⁺ and Fe⁵⁺. The corresponding quadrupole doublet relative areas are in compliance with the values

Composition	Space group	<i>a</i> , nm	<i>b</i> , nm	c, nm	β, °	$V/Z^*, nm^3$
$hrFe_{0.95}Mo_{0.05}O_{3-\delta}$ $Pm\overline{3}m$		0.3880(1)				0.0584
$SrFe_{0.8}Mo_{0.2}O_{3-\delta}$	$Pm\overline{3}m$	0.3911(2)				0.0598
$SrFe_{0.7}Mo_{0.3}O_{3-\delta}$	$P2_1/m$	0.5560	0.5557	0.7870	90.07	0.0608
$SrFe_{0.9}Al_{0.1}O_{3-\delta}$	$Pm\overline{3}m$	0.3882(6)				0.0585
$SrFe_{0.7}Al_{0.3}O_{3-\delta}$	$Pm\overline{3}m$	0.3900(4)				0.0593
$Sr_{0.97}Fe_{0.75}Al_{0.2}Mo_{0.05}O_{3-\delta}$	$Pm\overline{3}m$	0.3893(1)				0.0590
$Sr_{0.97}Fe_{0.7}Al_{0.2}Mo_{0.1}O_{3-\delta}$	Pm3m	0.3897(1)				0.0592

Table 1. Unit cell parameters for $SrFe_{1-x}Mo_xO_{3-\delta}$ and $Sr_{0.97}Fe_{0.8-x}Al_{0.2}Mo_xO_{3-\delta}$. The data is given for the materials after sintering and slow cooling in air, apart from $SrFe_{0.7}Mo_{0.3}O_{3-\delta}$, obtained after sintering in argon. The data for $SrFe_{0.95}Mo_{0.05}O_{3-\delta}$ [13] and $SrFe_{1-x}Al_xO_{3-\delta}$ [4] are given for comparison

*Z is the number of formula units in unit cell.

determined from spectra at 4 K (Table 2). All iron cations are predominantly in octahedral coordination with respect to oxygen, which corresponds to the calculated value of the oxygen nonstoichiometry ($\delta = 0.03$) under oxidative conditions, when the molybde-num oxidation state is 6+.

The Fe⁴⁺ localized state fraction in $SrFe_{0.8}Mo_{0.2}O_{3-\delta}$ is 25-26%, which is much larger than that in $Ln_{0.5}A_{0.5}FeO_{3-\delta}$ (8–15%) [24], it approaches the value of 20–21% obtained for La_{0.5}Sr_{0.5}Fe_{1-x}Al_xO_{3- δ} (x = 0.2 - 0.3) [25]. The replacing of iron with molybdenum or aluminum lowers the number of bonds (Fe3d-O2p) available for the electron transfer; hence, the electron state of at least part of the Fe⁴⁺ cations acquires a localized $\left| d^4 \right\rangle$ character restraining the charge disproportioning [35]. The localized Fe⁴⁺ concentration per formula unit is ~ 0.2 . This means that each Mo^{6+} cation lowers the delocalization state of 3delectrons of one Fe⁴⁺ cation. Indeed, when taking into account the Coulomb repulsion, we conclude that the probability to have more than one Fe⁴⁺ ion in the closest environment of Mo⁶⁺ is negligibly small.

The spectrum obtained at room temperature for $SrFe_{0.8}Mo_{0.2}O_3 = \delta$ annealed at 1223 K and $p(O_2) \approx 10^{-17}$ atm (Fig. 4b) resembles the one described earlier for the sample of identical composition, equilibrated at $p(O_2) = 10^{-4}$ atm and 1223 K [36]; all peaks are broadened, which is most likely due to the closeness to the magnetic ordering temperature. In this situation it is difficult to discover any details other then



Fig 2. X-ray diffraction patterns of $Sr_{0.97}Fe_{0.75}Al_{0.2}Mo_{0.05}O_{3-\delta}$ (a, c) and $Sr_{0.97}Fe_{0.7}Al_{0.2}Mo_{0.1}O_{3-\delta}$ (b) after annealing in air (a, b) and in 10% H₂-N₂-H₂O atmosphere (c).

the ground contribution. More accurate analysis is only possible for spectra obtained at much lower temperatures, when the peaks are narrower. For example, the spectrum taken at 4 K comprises six absorption

Composition/pretreatment	<i>Т</i> , К	Fe oxidation state and coordination	IS, $\langle IS \rangle$, mm/s	QS, ε, mm/s	$\langle B_{\rm hf} \rangle$, T	I, %
$SrFe_{0.8}Mo_{0.2}O_{3-\delta}$	4 3+		0.49	-0.02	49.4	66
annealed at $p(O_2) =$		4+ localized	0.10	-0.12	29.6	26
0.21 atm, $T = 1223$ K		5+	0.02	0.08	24.6	8
	295	3+	0.39	0.61	_	58
		4+ localized	0.02	0.30	_	25
		4+ delocalized	0.12	0.75	—	17
$SrFe_{0.8}Mo_{0.2}O_{3-\delta}$	4	3 + CN = 6, CN = 5	0.47	-0.01	53.4	92
annealed at $p(O_2) =$		3 + CN = 4	0.29	0.02	46.5	8
10^{-17} atm. $T = 1223$ K	295	3 + CN = 6, CN = 5	0.35	-0.01	45.9	91
· · · · · · · · · · · · · · · · · · ·		3 + CN = 4	0.21	0.01	39.0	9
$SrFe_{0.7}Mo_{0.3}O_{3-\delta}$	4	$3 + CN = 6^{**}$	0.49	-0.02	53.3	100
annealed at $p(O_2) =$	295	3 + CN = 6	0.36	-0.04	41.0	100
10^{-5} atm, $T = 1573$ K						

Table 2. Parameters* calculated from $SrFe_{1-x}Mo_xO_{3-\delta}M\ddot{o}ssbauer$ spectra recorded at 4 and 295 K

* IS is the isomer shift relative to metallic α -Fe at 295 K; QS and ε is the quadrupole splitting and quadrupole shift calculated for quadrupole doublets and magnetic sextupoles, respectively; $B_{\rm hf}$ is the hyperfine magnetic field; *I* is the relative area; CN is the iron cation coordination number with respect to oxygen.

**The states of Fe³⁺ with CN = 5 in SrFe_{0.7}Mo_{0.3}O_{3 - δ} are improbable because IS does not depend on B_{hf} in the sextupole distribution, whereas IS increased with the increasing of B_{hf} in the spectrum ground component for SrFe_{0.8}Mo_{0.2}O_{3 - δ} annealed in 10% H₂-N₂ environment.



Fig. 3. Mössbauer spectra taken at 4 K for $\text{SrFe}_{0.8}\text{Mo}_{0.2}\text{O}_{3-\delta}$ sample (a, b), annealed at 1223 K in air (a) and at $p(\text{O}_2) \approx 10^{-17}$ atm (b) and $\text{SrFe}_{0.7}\text{Mo}_{0.3}\text{O}_{3-\delta}$ sample annealed at $p(\text{O}_2) \approx 10^{-5}$ atm and 1573 K (c). Curves plotted over the experimental points are the sums of magnetic splitting distributions (shown somewhat higher for clarity sake). The hyperfine magnetic field (B_{hf}) probability (*P*) distributions are shown to the right for the corresponding spectra.

peaks with minor shoulders, more noticeable at larger rates (Fig. 3b). Therefore, unlike the work [36], the spectra were analyzed using two $B_{\rm hf}$ distributions. The least-area distribution has lower average IS and $B_{\rm hf}$ values typical of tetrahedrally coordinated Fe³⁺ in the perovskite oxides, whereas spectral parameters of the other distribution are characteristic of Fe^{3+} in octahedra (Table 2, [29, 37]). In the latter case, a proportionality between IS and B_{hf} was found, which shows that some sextets (with lower IS and B_{hf}) in the distribution can relate to the penta-coordinated Fe^{3+} . However, it seems to be impossible separating this contribution



Fig. 4. Mössbauer spectra taken at 295 K for SrFe_{0.8}Mo_{0.2}O_{3 - δ} sample (a, b) annealed at 1223 K in air (a) and at $p(O_2) \approx 10^{-17}$ atm (b) and SrFe_{0.7}Mo_{0.3}O_{3 - δ} sample annealed at $p(O_2) \approx 10^{-5}$ atm and 1573 K (c). Curves plotted over the experimental points are the sums of three doublets (a) or $B_{\rm hf}$ distributions (b, c) for clarity sake, the (a, b) spectra components are shown somewhat higher.

and the octahedral component. Even if Fe^{2+} is present in the reduced sample, its amount is too small to be detected using the Mössbauer spectroscopy. Nonetheless, even if the entire iron is supposed to have the oxidation state equal to 3+, while that of molybdenum is 6+, the oxygen nonstoichiometry δ must be 0.2. The tetrahedrally coordinated Fe³⁺ concentration calculated on the base of the above supposition for a ran-

RUSSIAN JOURNAL OF ELECTROCHEMISTRY Vol. 54 No. 6 2018



Fig. 5. Conductivity isotherms for $\text{Sr}_{1-y}(\text{Fe},\text{Al},\text{Mo})\text{O}_{3-\delta}$ ceramics at 1173 K (a) and $\text{Sr}_{0.97}\text{Fe}_{0.75}\text{Al}_{0.2}\text{Mo}_{0.05}\text{O}_{3-\delta}$ ceramics at 1023–1223 K (b). The data for $\text{SrFe}_{0.95}\text{Mo}_{0.05}\text{O}_{3-\delta}$ [13] and $\text{SrFe}_{0.7}\text{Al}_{0.3}\text{O}_{3-\delta}$ [4] are given for comparison. Solid lines in (b) correspond to results of data processing after the model described by equation (1); dashed lines correspond to straight lines with slope of +1/4 or -1/4 in the given coordinates.

dom distribution of oxygen vacancies in the crystal lattice, is ~5%, which is much less than that obtained from the Mössbauer spectroscopy data (Table 2). This result confirms the preference of the octahedral coordination for the molybdenum cations or points to the Mo⁵⁺ cation formation. By contrast, if all molybdenum cations have been reduced down to the oxidation state of 5+, the tetrahedron concentration at $\delta = 0.3$ would increase up to ~10%.

Shown In Figs. 3c and 4c are Mössbauer spectra of a SrFe_{0.7}Mo_{0.3}O₃₋₈ sample annealed at $p(O_2) \approx 10^{-5}$ atm and 1573 K. Unlike the reduced SrFe_{0.8}Mo_{0.2}O₃₋₈, the six absorption peaks in the spectrum taken at 4 K are symmetrical. Therefore, the SrFe_{0.7}Mo_{0.3}O₃₋₈ spectra were analyzed with a sole B_{hf} distribution. In contrast to the data obtained with SrFe_{0.8}Mo_{0.2}O₃₋₈, no B_{hf} dependence of IS exists in the distribution, while the average spectral parameters obtained are typical of the octahedrally coordinated Fe³⁺. This fact means not only the absence of tetrahedrons in the SrFe_{0.7}Mo_{0.3}O₃₋₈ crystal lattice but also the absence (or very small concentration) of pyramids there. The latter fact is in full compliance with the low oxygen nonstoichiometry level supposed for this composition; it also proves the Mo stabilizing role. As expected, no indication of iron cation in higher oxidation state is observed in SrFe_{0.7}Mo_{0.3}O_{3 - δ}. This means that both in oxidative and mild reductive conditions the *p*-type charge carrier concentration, hence, total conductivity (predominantly electronic one for these materials, as shown below) must decrease with the decreasing of *x* value in SrFe_{1 - x}Mo_xO_{3 - δ}, which is in full compliance with the experimentally measured conductivity.

In Fig. 5 isothermal dependences of the conductivity on $p(O_2)$ are given. They demonstrate specific features typical for the majority of ferrites [4, 5, 32], namely, decrease in the conductivity with the decreasing of $p(O_2)$ under oxidative conditions, as well as its increase under reductive conditions. Doping with aluminum suppressed the conduction at low $p(O_2)$ (Fig. 5a) owing to partial blocking of Fe-O-Fe bonds. The introducing of highly charged molvbdenum cations to the perovskite lattice produced opposite effect since they facilitate the iron cation reduction; moreover, they contribute to the *n*-type charge carrier transfer during the reduction, as it is suppose on the base of the Mössbauer spectroscopy data. The $SrFe_{0.7}Mo_{0.3}O_{3-\delta}$ conductivity under the anodic conditions is 10-40 S/cm at 1173 K, which is sufficient for the solid-oxide fuel cell electrode materials [2].

The Sr_{0.97}Fe_{0.75}Al_{0.2}Mo_{0.05}O_{3 - δ} conductivity isotherms were analyzed on the base of the standard model used in works [4, 5, 32]. In terms of this model, the conductivity is presented as a sum of partial hole conductivity (σ_p), electron (*n*-type) conductivity (σ_n), and oxygen-ion conductivity (σ_0):

$$\sigma = \sigma_{\rm O} + \sigma_n^{\circ} p\left({\rm O}_2\right)^{-1/4} + \sigma_p^{\circ} p\left({\rm O}_2\right)^{1/4}, \qquad (1)$$

where σ_p° and σ_n° are the partial *p*- and *n*-type conductivities at the oxygen unit partial pressure. The $p(O_2)$ -dependences of σ_p and σ_n are determined by the expressions for equilibrium constants between the molecular oxygen and the Fe^{4+/3+} and Fe^{3+/2+} redox couples that dominate the oxidative and reductive regions, respectively. The ionic conductivity in terms of the model is assumed being independent of $p(O_2)$ [4, 5, 32]. Results of calculations after the model describe adequately the experimental data in the *p*-*n* junction region (Fig. 5b). In more reductive atmospheres some deviation of the calculated curve from experimental points were observed, probably, owing to Mo⁶⁺ partial reduction to a state of lower charge, which affects the electron transfer mechanism, as well as a $p(O_2)$ dependence of σ_0 .

In Fig. 6 temperature dependences of the partial ionic conductivity are shown. In the previous papers

521

[4, 10] a strong effect of the ordered domain formation on the ionic transport of $Sr(Fe,Al)O_{3-\delta}$ was demonstrated. At lower temperatures migration of oxygen vacancies along the perovskite/brownmilletite interfaces begins limiting the oxygen transfer, which manifests itself in larger activation energy (Table 3). The introducing of 5% Mo to the strontium ferrite-aluminate crystal lattice suppresses the ordering processes effectively, owing to the presence of stable MoO₆ octahedra. As a result, at temperatures below 1073 K, that is, over the temperature range typical of the operation conditions for moderate-temperature solid oxide fuel cells, the oxygen-ion conductivity of Sr_{0.97}Fe_{0.75}Al_{0.2}Mo_{0.05}O_{3 - δ} exceeds that of $SrFe_{0.7}Al_{0.3}O_{3-\delta}$ and undoped $SrFeO_{3-\delta}$, despite the higher oxygen nonstoichiometry of the latter compositions. However, the replacement of >20%iron by the cations forming stable polyhedra (both octahedra and tetrahedra) with oxygen, clearly leads to a steep decrease in the mobility of oxygen vacancies even in the disordered perovskite phase. The probability of the vacancy formation in the Mo^{6+/5+} first coordination sphere is negligibly small, whereas the Al^{3+} cations partially block two vacancies each, thus forming a stiff defect complex. Molybdenum doping lowers the oxygen vacancy total concentration as well, therefore, the ion transfer in $\text{SrFe}_{1-x}\text{Mo}_x\text{O}_{3-\delta}(x \ge 0.05)$ on the whole is less pronounced than in the Al-containing analogues.

In Figs. 7a and 7b we present dependences of the oxygen flux *j* and specific oxygen permeability $J(O_2)$ of gas-tight $Sr_{0.97}Fe_{0.75}Al_{0.2}Mo_{0.05}O_{3-\delta}$ -membranes with different thickness (*d*) on the oxygen partial pressure drop p_2/p_1 . According to Wagner equation, the rate of



Fig. 6. Temperature dependences of the $Sr_{0.97}Fe_{0.75}Al_{0.2}Mo_{0.05}O_{3-\delta}$ partial ionic conductivity obtained from the conductivity isothermal dependences or from results of the oxygen permeability measurements. The data for SrFe_{1-x}Al_xO_{3-\delta} [4] are given for comparison.

oxygen ion transfer across the membrane phase must be inversely proportional to the membrane thickness. However, at temperatures below 1223 K the *j* value is practically independent of *d*, which points to the dominating role of the oxygen surface exchange kinetics, which decreased at a heating and increased following $p(O_2)$ decrease. The higher activation energy of the oxygen surface exchange as compared with the oxygen bulk diffusion is in reasonable agreement with the behavior observed for SrFe_{1 - x}Al_xO_{3 - \delta} [4]. Because the quantity $J(O_2)$ is by definition proportional to the

Table 3. Thermal expansion coefficients and ionic conductivity activation energy calculated from isothermal $p(O_2)$ -dependences of conductivity. The data for SrFe_{1-x}Al_xO_{3-\delta} [4] are given for comparison

Composition		Thermal expansion	Ionic conductivity		
Composition	Atmosphere	<i>Т</i> , К	TEC × 10^{6} , K ⁻¹	<i>Т</i> , К	$E_{\rm a}$, kJ/mol
$Sr_{0.97}Fe_{0.75}Al_{0.2}Mo_{0.05}O_{3-\delta}$	Air	873-1223	27.1 ± 0.6	973-1223	87 ± 5
	Argon	873-1223	17.6 ± 0.2		
$Sr_{0.97}Fe_{0.7}Al_{0.2}Mo_{0.1}O_{3-\delta}$	Air	303-873	15.4 ± 0.1		
		873-1223	25.3 ± 0.1		
	Argon	873-1223	16.6 ± 0.3		
$SrFe_{0.8}Mo_{0.2}O_{3-\delta}$	Air	303-873	14.1 ± 0.1		
		873-1223	22.7 ± 0.1		
$SrFe_{0.7}Mo_{0.3}O_{3-\delta}$	Argon	873-1223	14.2 ± 0.5		
	$10\% H_2 - N_2$	873-1223	14.5 ± 0.5		
$SrFe_{0.9}Al_{0.1}O_{3-\delta}$	Air	373-823	16.4 ± 0.4		
		823-1273	31.9 ± 0.3		
$SrFe_{0.7}Al_{0.3}O_{3-\delta}$	Air	373–923	15.4 ± 0.1	1073-1223	78 ± 11
		923-1273	23.0 ± 0.1	973-1073	157



Fig. 7. Isothermal dependences of oxygen fluxes (a) and specific oxygen permeability (b) across dense $SrFe_{0.8}Mo_{0.2}O_3 = \delta$ and $Sr_{0.97}Fe_{0.75}Al_{0.2}Mo_{0.05}O_3 = \delta$ ceramic membranes of different thickness.

(*jd*) product [38], it must be independent of the membrane thickness at insignificant limitations of the surface exchange and increase with the increasing of *d* when the exchange effect increased. At 1223 K both quantities [*j* and $J(O_2)$] depend on *d*, which points to a comparability of the oxygen diffusion and surface



Fig. 8. Isothermal dependences of ionic conductivity and the sum of reciprocal constants of surface exchange for $Sr_{0.97}Fe_{0.75}Al_{0.2}Mo_{0.05}O_3 - \delta$, calculated on basis of the model described in [31], at $p(O_2) = 0.21$ atm.

exchange. The situation allows estimating the ambipolar conductivity that in this case equals ionic one, as well as the sum of the surface exchange reciprocal constants $(k_1 \text{ and } k_2)$, by using the model described earlier [31].

Results of the calculations (Fig. 8) demonstrate increase in the Sr_{0.97}Fe_{0.75}Al_{0.2}Mo_{0.05}O_{3 - δ} ionic conductivity with the increasing of the oxygen pressure drop caused by the oxygen vacancy formation as a result of reduction. For the same reason, the ionic conductivity value obtained by the extrapolating of the data to zero pressure drop (which corresponds to σ_0 in air) appears being lower than that calculated from the isothermal dependences of the total conductivity (Fig. 6). Nonetheless, Sr_{0.97}Fe_{0.75}Al_{0.2}Mo_{0.05}O_{3 - δ} demonstrates rather high oxygen transfer level; at 1223 K and the oxygen pressure drop $p(O_2)$ approaching zero the σ_0 and $(k_1^{-1} + k_2^{-1})^{-1}$ values are 0.15 S/cm

and 5×10^{-7} mol/(s cm²), respectively. For comparison, similar parameters found for La_{0.9}Sr_{0.1}Fe_{0.9}Ni_{0.1}O_{3- δ}, are 1.5 × 10⁻³ S/cm and ~4 × 10⁻⁹ mol/(s cm²), respectively [27].

Apart of the ionic and electron transport level, one of the most important criteria in the choice of electrode materials are thermomechanical characteristics. In dilatometric curves a steep TEC growth occurs: from ~15 × 10⁻⁶ K⁻¹ at temperatures below 900 K up to $(20-30) \times 10^{-6}$ K⁻¹ at further heating (Fig. 9, Table 3). The oxygen removal from crystal lattice, in particular, caused by heating results in growth of both the radius of *d*-element cations and the inter-cation Coulomb repulsion. This is in good agreement with the Sr_{0.97}Fe_{0.8 - x}Al_{0.2}Mo_xO_{3 - δ} and SrFe_{1 - x}Al_xO_{3 - δ} isothermal expansion in argon atmosphere, which is as large as 0.2–0.5% (Fig. 10a, Table 4). As expected, the level of bulk changes during isothermal redox-cycling correlates with the iron content.



Fig. 9. Dilatometric curves of $\text{Sr}_{1-y}(\text{Fe,Al,Mo})O_{3-\delta}$ ceramic samples taken in the constant heating regime in air. The data for $\text{SrFe}_{1-x}\text{Al}_xO_{3-\delta}$ [4] are given for comparison.

RUSSIAN JOURNAL OF ELECTROCHEMISTRY Vol. 54 No. 6 2018

The high values of the average TEC at temperatures >873 K (Table 3), occurring because of the chemical contribution to the expansion, somewhat limit the possibility of the applying anodic layers without additional modification, such as composite formation. In this respect the most advantageous is the composition $\text{SrFe}_{0.7}\text{Mo}_{0.3}\text{O}_{3-\delta}$ whose TEC is 14.5×10^{-6} K⁻¹ in the Ar and 10% H₂ atmospheres. However, the material oxidation leads to its significant expansion, which comes to ~1.7% after switching from 10% H_2 to argon environment (Fig. 10b). This behavior is uncharacteristic of perovskites and may be associated with phase transformation. The molvbdenum cation partial oxidation to Mo⁶⁺ is likely to be accompanied with formation of microdomains including impurity phases or structure distortions that cannot be detected by the X-ray diffraction analysis. Their formation can result in the occurrence of local excessive strains that can, if exceeded some threshold value, initiate microcrack irreversible formation, followed by subsequent changes in the bulk. Irrespective of particular mechanism of the expansion observed, this effect should be taken into consideration in the anodic layer producing and testing. Nonetheless, owing to the TEC moderate values (Table 3) coupled with the relatively large conductivity under reductive conditions (Fig. 5), it is the $SrFe_{0.7}Mo_{0.3}O_{3-\delta}$ composition that has been chosen for the studying of solid oxide fuel cell model anodes.

Polarization studies proved rather high electrochemical activity of the $SrFe_{0.7}Mo_{0.3}O_{3-\delta}$ porous anodic layer contacting a $(La_{0.9}Sr_{0.1})_{0.98}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ solid electrolyte (Figs. 11 and 12). The reproducibility of results was proved by measurements with several series of samples (insert in Fig. 11). In different series of measurements the polarization resistance varies within 0.6–0.8 Ω cm² at 1073 K in 10%H₂–N₂–H₂O atmosphere, which is 1.5–2 times lower than that for the (La,Sr)(Cr,Fe)O_{3 - δ}- or (La,Sr)(Mn,Ti)O_{3 - δ}based anodes under similar conditions [28, 33, 39]. Thus obtained characteristics are comparable with those of many Mo-containing anode materials; we



Fig. 10. Temperature dependences of relative expansion for $Sr_{0.97}Fe_{0.8-x}Al_{0.2}Mo_xO_{3-\delta}$ (a) and $SrFe_{0.7}Mo_{0.3}O_{3-\delta}$ (b) ceramics.

recall that in this work diluted (down to 10%) hydrogen was used as a fuel, which resulted, in particular, in hampered fuel diffusion. This factor manifested itself in the tending of the polarization curves toward limiting current.

As has been noted above, the occurance of phase transformations and the bulk changes during the oxidation associated therewith restricts significantly the $SrFe_{0.7}Mo_{0.3}O_{3-\delta}$ usage as solid oxide fuel cell anode. At the same time, the redox-stability tests did not reveal any degradation of electrode characteristics after 20-h-long oxidation in argon with subsequent

Т, К	$(L_{\rm Ar}-L_{\rm air})/L_{\rm air},$ %					
	$SrFe_{0.7}Al_{0.3}O_{3-\delta}$	$Sr_{0.97}Fe_{0.75}Al_{0.2}Mo_{0.05}O_{3-\delta}$	$Sr_{0.97}Fe_{0.7}Al_{0.2}Mo_{0.1}O_{3-\delta}$			
1223	0.16	0.20	0.22			
1173	0.22	0.24	0.26			
1123	0.24	0.28	0.29			
1073	0.33	0.32	0.34			
1023	_	0.38	0.38			
973	_	0.43	0.43			
923	_	0.48	0.48			

Table 4. Expansion of $Sr_{0.97}Fe_{0.8-x}Al_{0.2}Mo_xO_{3-\delta}$ and $SrFe_{0.7}Al_{0.3}O_{3-\delta}$ ceramics on their reduction in argon atmosphere ($p(O_2) \approx 10^{-5}$ atm) with respect to the length in air at the shown temperature



Fig. 11. Current-density dependences of anodic overvoltage for porous electrode layer of $SrFe_{0.7}Mo_{0.3}O_3 = \delta$ deposited onto $(La_{0.9}Sr_{0.1})_{0.98}Ga_{0.8}Mg_{0.2}O_3 = \delta$ electrolyte with a $Ce_{0.8}Gd_{0.2}O_2 = \delta$ sublayer, measured in $10\% H_2 - N_2 - H_2O$ atm over 873–1073 K temperature range. Insert: dependences obtained for two identical samples at 1073 K.

50-h-long anodic polarization (Fig. 12). The rather high electrochemical activity along with stability with respect to moderate redox-cycling make the $SrFe_{0.7}Mo_{0.3}O_{3-\delta}$ -based materials attractive as solid oxide fuel cell anodes.

CONCLUSIONS

Mo-doping into $Sr(Fe,Al)O_{3-\delta}$ increased the resistance of the material against ordering in the oxygen sublattice, however, decreased its stability in oxidative environments, which results in impurity phase formation, as well as significant bulk changes after oxidation. The Mo and Al introducing to strontium ferrite decreased changes of the oxygen nonstoichiometry during the temperature and redox-cycling, which results in the decreasing of thermal and chemical expansion and the *p*-type electronic conductivity. At that, the Mo-doping facilitates significantly the *n*-type electron transport in reductive environments. Despite a decrease in the oxygen vacancy concentration, moderate doping with molybdenum has a positive effect on the oxygen-ion conductivity at temperatures below 1073 K when the effect of ordering processes in the oxygen sublattice increased. The oxygen-ion conduc-



Fig. 12. Time dependences of overvoltage at the $SrFe_{0.7}Mo_{0.3}O_{3-\delta}$ anode for current density of 100 mA/cm² (a), polarization resistance (b), and Ohmic resistance relative change (c) taken in galvanostatic regime at 1073 K under succession of gas environments 10% $H_2-N_2-H_2O \rightarrow Ar \rightarrow 10\% H_2-N_2-H_2O$.

525

tivity of the Sr_{0.97}Fe_{0.75}Al_{0.2}Mo_{0.05}O_{3 - δ} gas-tight ceramics is determined by both oxygen bulk diffusion and the surface oxygen exchange kinetics; the cooling and decreasing of $p(O_2)$ increased the role of the latter factor. Owing to the SrFe_{0.7}Mo_{0.3}O_{3 - δ} solid solution rather high electron conductivity (38 S/cm at $p(O_2) = 10^{-17}$ atm and T = 1173 K) and moderate TEC value (14.5 × 10⁻⁶ K⁻¹ in Ar and 10% H₂ environments), the porous anodic layer on its base demonstrated relatively high electrochemical activity and acceptable stability with respect to redox-cycling. When contacting a lanthanum-gallate-based solid electrolyte, the material shower polarization resistance of 0.6 Ω cm² and overvoltage of 156 mV at a current density of 200 mA/cm² in 10% H₂ at 1073 K.

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