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# PEROVSKITE-LIKE $(La_{0.75}Ca_{0.25})_{0.95}Cr_{1-x}Fe_xO_{3-\delta}$ AS POTENTIAL ELECTRODE MATERIALS FOR SYMMETRIC SOLID OXIDE FUEL CELLS

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***Abstract:*** *The study is focused on the synthesis and characterization of $(La_{0.75}Ca_{0.25})_{0.95}Cr_{1-x}Fe_xO_{3-\delta}$ (x = 0.3 - 0.9)perovskites as potential materials for solid oxide fuel cell (SOFC) cathode and anode. These materials possessanorthorhombically-distorted structure at room temperature whilst heating above 800-1100 K induces reversible transformation into the rhombohedral symmetry. The transition temperature increases with iron content. The linear thermal expansion coefficients vary in the range (10.5-11.1)×$10^{-6}$ $K^{-1}$ and slightly grow on Fe-doping.The volume changes upon reduction are within 0.16%. The electronic conductivity exhibits a thermally-activated character and increases on Fe introduction, in particular due to an enhancement of the number of sites available for electronic transfer; this trend is observed both under oxidizing and reducing conditions. The low level of the electronic conductivity seems to be responsible for an insufficient electrochemical activity of $(La_{0.75}Ca_{0.25})_{0.95}Cr_{1-x}Fe_xO_{3-\delta}$-based cathodes.Under anodic conditions, other factors, such as electrode microstructure or surface-related properties, affect the electrochemical behavior.*

***Keywords:*** *perovskite, phase transition, thermal expansion, chemical expansion, total conductivity, polarization resistance.*
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## Introduction

The reduction of operating temperature of Solid Oxide Fuel Cells (SOFC) and a partial replacement of hydrogen by other fuels, generally produced from hydrocarbon-containing sources,requires development of novel functional materials capable to operate adequately under necessary conditions. Conventional Ni-based composites used as SOFC anodes suffer from microstructural degradation with time or upon redox cycling and possible coking in hydrocarbon- or carbon monoxide-enriched atmospheres [1-3]. Chromite-based perovskites are considered to be possible alternative anode materials due to their high stability under reducing conditions and moderate volume and microstructural changes on reduction which decreases the risk of the electrode cracking or delamination from the solid electrolyte. However, significant limitation of $LaCrO_{3-\delta}$ and related materialsis their insufficient conductivity, especially under reducing conditions, and low electrochemical activity towards oxidation processes which requires addition of surface-active agents into the anode layer [2, 4-6].

In recent 15-20 years it was demonstrated that appropriate doping in A- or B-sublattice may substantially improve the electrode properties of chromites both in oxidizing and reducing atmospheres. The latter factor is attractive for their simultaneous utilization as cathodes and anodes in symmetrical SOFCswhere both electrodes are prepared from the same material which simplifies the procedure of electrode coating and subsequent firing [5, 7-11]. The basic strategy of substitution in B-sublattice relates to introducing cations with variable oxidation state or oxygen coordination (Mn, Fe, Co, Ni, V) which makes possible generation of additional charge carriers and channels of their transfer, improvement of the oxygen ionic conductivity due to higher concentration of oxygen vacancies or modifying the surface-related properties. In particular, (La,Sr)(Cr,Mn)$O_{3-\delta}$perovskites are considered to be among the most active Ni-free anode materials due tocomparatively high performance in$H_2$, hydrocarbons, alcohols and other fuels [5, 11-14].Owing to the high stability and acceptable conductivity in both oxidizing and reducing atmospheres, this material has a great potential for utilization as both electrodes of symmetrical SOFCs [8, 12, 15].

Fe-doped chromites represent another attractive group of perovskite-based anodes since these materials combine both acceptable stability in the anode atmosphere and the conductivity level necessary for ensuring good anode properties. In particular, in [7, 8] the performance of (La,Sr)(Cr,Fe)$O_{3-\delta}$ anodes was demonstrated to be superior as compared to that of Mn-substituted analogues measured under similar conditions, while the low-temperature stabilization of the oxygen nonstoichiomentryenablesto preserve a comparatively high conductivity level (40-50 S/cm) even in reducing atmospheres. At the same time, (La,Sr)(Cr,Fe)$O_3$-based anodes showed moderate performance in hydrocarbon-, CO-, $H_2S$- and even $PH_3$-containing fuels, with more stable operation in comparison with the conventional Ni-based anodes [10, 16-19]. However, Fe-doped chromites are reported to exhibit an enormous expansivity (>1% in linear scale [7]) upon reduction which may be problematic for long-term utilization of the corresponding cell.

Previous studies on(La,Sr,Ca)$FeO_{3-\delta}$perovskites showed that a partial or complete substitution of Ca for Sr allows to modify the functional properties, particularly, to reduce the thermal and chemical expansion and improve, to some extent, the phase stability. Excessive amount of Ca is undesirable since it may lead to ordering of oxygen vacancies in the crystal lattice deteriorating the transport properties; this effect is substantially suppressed for Cr-containing ferrites [20-22]. Taking the above information into account, the present work is focused on evaluation of $(La_{0.75}Ca_{0.25})_{0.95}Cr_{1-x}Fe_xO_{3-\delta}$ ($0.3 \le x \le 0.9$) perovskites as potential cathode and anode materials of symmetrical SOFCs.

## Objective of the article

The primarily objectiveof the work is to study the phase and structural stability, transport and thermomechanicalproperties of $(La_{0.75}Ca_{0.25})_{0.95}Cr_{1-x}Fe_xO_{3-\delta}$ perovskites and evaluate the electrochemical activity of corresponding cathodes and anodes with a special emphasis on the relationships between the transport, electrochemical and structural behavior of these materials.

## Experimental

Synthesis of $(La_{0.75}Ca_{0.25})_{0.95}Cr_{1-x}Fe_xO_{3-\delta}$(LCCF) solid solutions was carried out with glycine-nitrate processing (GNP) from $La(NO_3)_3\times6H_2O$, $Ca(NO_3)_2$, $Cr(NO_3)_3\times9H_2O$ and $FeC_2O_4\times2H_2O$ preliminary dissolved in 20 mL of concentrated nitric acid as precursors. The precise molar mass of the starting reactants which might be affected by possible water losses or other compositional changes with timewas determined with the thermo-gravimetric analysis (TGA) by high-temperature transformation of the corresponding precursor into $La_2O_3$, CaO or Fe in air or $H_2$-Ar atmosphere until the constant mass was achieved. The water content was calculated from relative mass changes. The details of the GNP method may be found elsewhere ([7, 12] and references cited). The synthesized powder was consecutively ground in a mortar and annealed in a furnace at 1073 – 1573 K. In order to obtain dense ceramics, the annealed powderswereuniaxially compacted in a press mould under 100-150 MPa pressure followed by sintering at 1673 – 1743 K in air.

X-ray diffraction (XRD) analysis was carried out with a Siemens D-500-BRAUNdiffractometerusing of Cu$K_\alpha$ irradiation in the 2θ range of 20-80ºC. The analysis of phase composition and calculation of lattice parameters was made with the use of Match andPowderCell 2.4software. Studies oftransport and thermo-mechanical properties were performed on rectangular-shaped bars obtained by cutting and subsequent polishing of ceramic pellets. The total conductivity was measured on direct current using a 4-probe technique in a laboratory-made tubular furnace in a flow of the required gas; the oxygen partial pressure ($p(O_2)$) was controlled using an electrochemical oxygen sensor inserted into the tube. Thermomechanicalmeasurements were fulfilled in a vertical dilatometer Linseis V75 equipped with an electrochemical pump and sensor to ensure the necessary oxygen content in the gas atmosphere. The methodology of dilatometric measurements and calculation of the thermal/chemical expansion coefficients is discussed in [12, 22] and referenced therein.

Electrochemical properties were studied on symmetrical cells LCCF / LDC / LSGM / LDC / LCCF, where LSGM and LDC correspond to $(La_{0.9}Sr_{0.1})_{0.98}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ and $Ce_{0.6}La_{0.4}O_{2-\delta}$ used as the solid electrolyte and protective sublayer, respectively. For deposition of porous electrode layers on LSGM pellet (thickness 0.7-1.0 mm, area 0.4 – 0.5 $cm^2$) a laboratory-made print-screening device was used. Each coating step was followed by firing the applied layers in air at 1473 K. The polarization resistance measurements were carried out by a 2-electrode method in a symmetrical configuration without applying current. Pt meshes were used as current collectors; no additional modifications of the electrodes such as preparation of composites, impregnation with catalytically active agents or coating with a metallic paste, were undertaken within the framework of the present study. The studies were carried out in a tubular furnace in $O_2$-air-Ar or $H_2$-Ar-$H_2O$ mixtures using an oxygen sensor forp($O_2$) control. The impedance spectra were collected using a potentio-/galvanostate MetrohmAutolab (PGSTAT302N)in 1 MHz – 5 mHz frequency range with AC amplitude of 50-100 mV. The microstructure of the electrode layers was studied using a LEO SUPRA 50VP (Carl Zeiss, Germany) scanning microscope.

## Results and discussion

Fig. 1 shows XRD patterns of as-prepared $(La_{0.75}Ca_{0.25})_{0.95}Cr_{1-x}Fe_xO_{3-\delta}$.

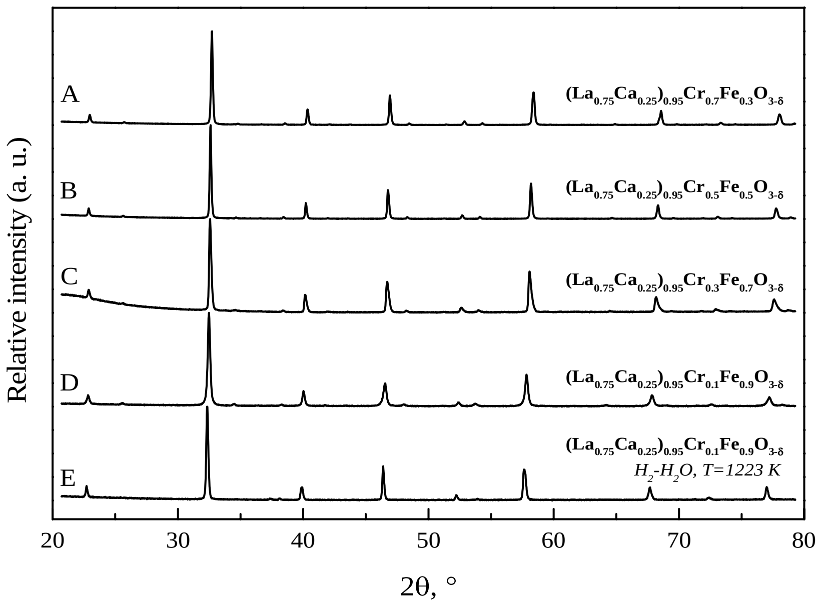



**Fig. 1**. XRD patterns of $(La_{0.75}Ca_{0.25})_{0.95}Cr_{1-x}Fe_xO_{3-\delta}$ perovskites, slowly cooled in air (A-D) and annealed in humidified 4% $H_2$-Ar (E).

All the materials synthesized are nearly single-phase perovksites with the orthorhombic structure while reduction of Fe-enriched compositions promotes the transition into the cubic symmetry.Doping with Fe increases the cell parameters (Table 1) in accordance with larger radii of $Fe^{3+}$ and $Fe^{4+}$cations in comparison with the chromium analogues [23]. Moreover, substitution of iron for chromium might enhance the oxygen deficiency leading to an increase of ratio of 3-fold charged cations to 4-fold ones; this fact requires verification by measuring the oxygen content under ambient conditions or studying the cation state by X-ray photoelectron spectroscopy, Mössbauer spectroscopy or other appropriate techniques. The same factors might be responsible for slight increment of the thermal expansion coefficients with iron content (Fig. 2, Table 1).

**Table 1.** Unit cell parameters, thermal expansion coefficients and chemical expansion on reductionof air-prepared $(La_{0.75}Ca_{0.25})_{0.95}Cr_{1-x}Fe_xO_{3-\delta}$ ceramics in CO-$CO_2$ atmospheres($p(O_2)$ = $10^{-12}$ – $10^{-20}$atm)

| Composition | a, Å | b, Å | c, Å | V, Å$^3$ | TEC×$10^6$, $K^{-1}$ | $\frac{L_{air}-L_{CO/CO_2}}{L_{air}}$, % *(T, K)* |
|---|---|---|---|---|---|---|
| $(La_{0.75}Ca_{0.25})_{0.95}Cr_{0.7}Fe_{0.3}O_{3-\delta}$ *as-prepared in air* | 5.477(2) | 7.745(2) | 5.465(2) | 231.8 (2) | 10.5±0.1 | 0.13*(1223)* 0.16*(973)* |
| $(La_{0.75}Ca_{0.25})_{0.95}Cr_{0.5}Fe_{0.5}O_{3-\delta}$ *as-prepared in air* | 5.490(2) | 7.765(2) | 5.479(2) | 233.5 (2) | 10.8±0.1 | 0.13*(1223)* 0.14*(973)* |
| $(La_{0.75}Ca_{0.25})_{0.95}Cr_{0.3}Fe_{0.7}O_{3-\delta}$ *as-prepared in air* | 5.504(2) | 7.787(2) | 5.487(2) | 235.2 (2) | 10.7±0.1 | 0.11*(1223)* 0.10*(973)* |
| $(La_{0.75}Ca_{0.25})_{0.95}Cr_{0.1}Fe_{0.9}O_{3-\delta}$ *as-prepared in air* | 5.527(2) | 7.833(2) | 5.524(2) | 239.2 (2) | 11.1±0.1 | |
| $(La_{0.75}Ca_{0.25})_{0.95}Cr_{0.1}Fe_{0.9}O_{3-\delta}$ *reduced in wet $H_2$-Ar, 1273 K* | 3.914(2) | | | 1/4×239.8 (4) | | |

*Cell parameters correspond to the orthorhombic (Pnma) or cubic (Pm3m) structure for samples prepared in air or annealed in wet $H_2$-Ar, respectively. $p(O_2)$ in CO-$CO_2$ mixture was ~$10^{-13}$atm (1223 K) and ~$10^{-19}$atm (973 K). TEC values correspond to the 300-1273 K temperature range in air.*

It should be noticed that the effect of iron content on the chemical expansion is different from common trends known for ferrites where replacement of iron with foreign cations generally reduces oxygen losses and resultant volume changes [7, 24, 25]. The abnormal behavior detected in the study might be associated with the structural transformation discussed below which occur in the considered temperature range, or with a comparatively high oxygen non-stoichiometry for Fe-enriched compositions in air at elevated temperatures, and subsequent reduction might lead to somewhat lower changes of oxygen content as compared to that of nearly stoichiometric compositions with lower iron content. One should also take into account that the difference in the expansivity is rather insignificant and comparable to the measurement uncertainty. Irrespective of origins of the unusual behavior, the volume changes on reduction in CO-$CO_2$ atmosphere are 0.10-0.16% in the linear scale which is substantially lower as compared to the values reported for $(La_{0.75}Sr_{0.25})_{0.95}Cr_{1-x}Fe_xO_{3-\delta}$[7] and much closer to the typical level of isothermal expansion of chromite-based materials upon reduction [12, 24-26].

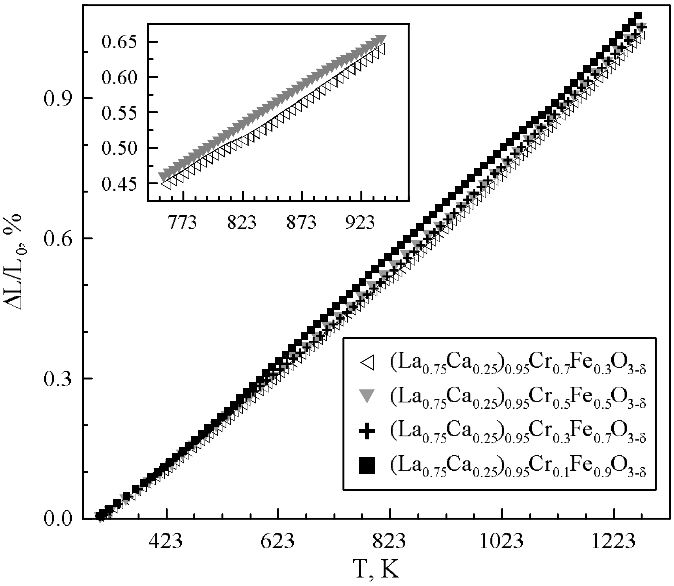



**Fig. 2.** Relative length changes of $(La_{0.75}Ca_{0.25})_{0.95}Cr_{1-x}Fe_xO_{3-\delta}$ ceramics on cooling in air. The inset shows zoomed view of the dilatometric curves in the 743-953 K temperature range.

A peculiarity of the studied materials is the presence of a kink on the dilatometric curves (inset in Fig. 2) which is reproducible upon heating and cooling observableboth in air and argon atmospheres. In accordance with literature data [4, 26-30], this behavior might be associated with reversible 1st order transition of the orthorhombic structure into the rhombohedral one. For the title materials, this effect occurs at significantly higher temperatures as compared to some other chromitesshown in Table 2 which might originate from an increase of transition temperatures upon Ca- or Fe-doping; the effect of Fe introduction on the transition temperature confirms this suggestion. Verification of the structural changes requires high-temperature XRD analysis; nevertheless, from the viewpoint of potential application of the materials as SOFC electrodes, the negligible volume changes induced by this effect as well as moderate chemical expansivity and the values of TECs comparable to those of typical electrolytes [31] suggest an adequate mechanical compatibility between the electrochemical cell components.

**Table 2.** Comparison of the phase transition temperatures for selected $LaCrO_3$-based perovskites

| Composition | $T_{ph.trans}$, K | Reference |
|---|---|---|
| $LaCrO_{3-\delta}$ | 520 | [27, 28] |
| | 560 | [29] |
| $La_{0.9}Ca_{0.1}CrO_{3-\delta}$ | 580 | [27] |
| $La_{0.9}Sr_{0.1}CrO_{3-\delta}$ | 340 | [27] |
| $LaCr_{0.9}Mg_{0.1}O_{3-\delta}$ | 600 | [27] |
| $LaCr_{0.8}Mg_{0.2}O_{3-\delta}$ | 620 | [27] |
| $(La_{0.9}Sr_{0.1})_{0.98}Cr_{0.9}Mg_{0.1}O_{3-\delta}$ | 336±10 | [26] |
| $(La_{0.75}Ca_{0.25})_{0.95}Cr_{0.7}Fe_{0.3}O_{3-\delta}$ | 815±5 | This work |
| $(La_{0.75}Ca_{0.25})_{0.95}Cr_{0.5}Fe_{0.5}O_{3-\delta}$ | 910±5 | This work |
| $(La_{0.75}Ca_{0.25})_{0.95}Cr_{0.1}Fe_{0.9}O_{3-\delta}$ | 1080±5 | This work |
| $(La_{0.9}Sr_{0.1})_{0.98}Cr_{0.8}Mg_{0.1}Fe_{0.1}O_{3-\delta}$ | 405±10 | [26] |
| $(La_{0.9}Sr_{0.1})_{0.98}Cr_{0.6}Mg_{0.1}Fe_{0.3}O_{3-\delta}$ | 545±5 | [26] |
| $LaCr_{0.9}Ni_{0.1}O_{3-\delta}$ | 640 | [28] |
| $LaCr_{0.8}Ni_{0.2}O_{3-\delta}$ | 670 | [28] |
| $(La_{0.9}Sr_{0.1})_{0.95}Cr_{0.85}Mg_{0.1}Ni_{0.05}O_{3-\delta}$ | 360±10 | [30] |

Increasing iron content leads to an enhancement of the total conductivity; this trend is observed both in air and in wet $H_2$-Ar (Fig. 3)and is opposite to the results obtained for$(La_{0.75}Sr_{0.25})_{0.95}Cr_{1-x}Fe_xO_{3-\delta}$[7]. Whereas in the latter case the negative effect of iron content on the conductivity was attributed toits essentially constant oxidation state irrespective to Cr:Fe ratiowhich suggests exclusion of Fe species from participation in the electron transfer, in the studied materials the conductivity seems to be governed by other factors.

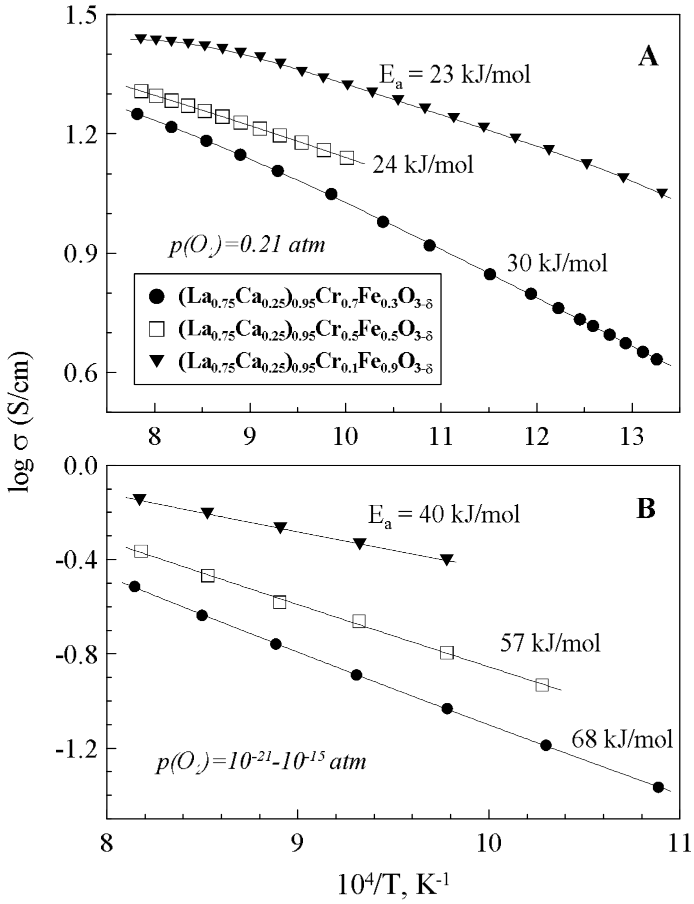
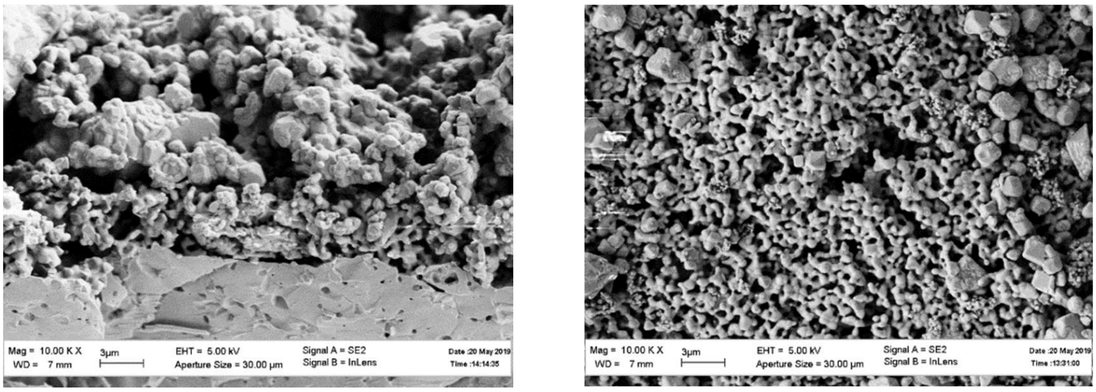



**Fig. 3.** Temperature dependencies of the total conductivity of $(La_{0.75}Ca_{0.25})_{0.95}Cr_{1-x}Fe_xO_{3-\delta}$ ceramics in air (A) and in wet 4% $H_2$-Ar mixture (B). The activation energies of the total conductivity are marked near the corresponding data.

It should be noted that similar contradictions are quite typical for chromite-based materials [5, 32-35] and may be associated with specific factors such as large differences in energy levels between $Cr^{3+}$ and guest cations significantly affecting the probability of residence of charge carriers on these atoms or percolation between the species with close energies which is affected by oxygen nonstoichiometry, lattice symmetry, cell parameters, etc. The conductivity of $(La_{0.75}Sr_{0.25})_{0.95}Cr_{1-x}Fe_xO_{3-\delta}$exhibits a thermally-activated character; the activation energies decrease with iron content (Fig. 3) suggesting that the electronic transport of presumably p-type electronic charge carriers proceeds more rapidly via Fe-O-Fe channels. For x=0.9, a slight tendency towards theconductivity maximum typical for ferrite-based materials [21, 24] is observed in air at high temperatures (Fig. 3a) associated with the increase of oxygen nonstoichiometry leading to lower concentration of charge carriers and break of conductive channels. The conductivity varies in the range of 10-30 and 0.1-1 S/cm under cathode and anode conditions, respectively. Obviously, this level is insufficient for an adequate operation ofthe corresponding electrodes, especially in reducing atmospheres which requires an improvement of current collection, for example, by fabrication of composites with metallic phases.

Electrode layers $(La_{0.75}Ca_{0.25})_{0.95}Cr_{0.7}Fe_{0.3}O_{3-\delta}$ presented in Fig. 4 show a nonuniform porosity and particle size distribution, although one should not exclude a possibility of microstructural changes during the electrode testing. No cracks in the electrode layer or its delamination from the electrolyte were detected.



**A** **B**

**Fig. 4.** Cross-section (A) and top view (B) of a cell with $(La_{0.75}Ca_{0.25})_{0.95}Cr_{0.7}Fe_{0.3}O_{3-\delta}$ electrode layer after testing under anode conditions.

Fig. 5illustrates examples of the impedance spectra for $(La_{0.75}Ca_{0.25})_{0.95}Cr_{0.7}Fe_{0.3}O_{3-\delta}$ and $(La_{0.75}Ca_{0.25})_{0.95}Cr_{0.3}Fe_{0.7}O_{3-\delta}$ collected under cathodic and anodic conditions. For both electrodes, the Ohmic resistance decreases as the oxygen partial pressure rises in accordance with the electronic conductivity of the electrode materials. The polarization losses show a correlation with the content of the electrochemically-active component in the gas mixture, i.e. $O_2$ or $H_2$ for cathode and anode conditions, respectively. While these effects are similar for both electrode compositions, the impact of Cr:Fe ratio differs for various testing conditions. $(La_{0.75}Ca_{0.25})_{0.95}Cr_{0.3}Fe_{0.7}O_{3-\delta}$ cathode exhibits lower Ohmic and polarization resistance as compared to the material with higher Cr content; this trend is not surprising taking into account better conductivity of Fe-rich compositions (Fig. 3) and well-known improved catalytic activity of ferrite-based compositions in redox processes [36-38].The low-frequency arc for the Fe-enriched cathode is more suppressed (Fig. 5D) than that for $(La_{0.75}Ca_{0.25})_{0.95}Cr_{0.7}Fe_{0.3}O_{3-\delta}$ which may be associated withmicro-structural factors or a mechanism of oxygen adsorption or surface diffusion promoted by the higher electronic and ionic conductivity. However, in reductive atmospheresthe introduction of iron into the electrode composition has a negative effect even despitehigher conductivity in comparison with $(La_{0.75}Ca_{0.25})_{0.95}Cr_{0.7}Fe_{0.3}O_{3-\delta}$ and negligible difference of the thermal and chemical expansion. It should be remembered that the phase composition of $(La_{0.75}Ca_{0.25})_{0.95}Cr_{0.3}Fe_{0.7}O_{3-\delta}$ annealed insimilar $H_2O$-$H_2$-Ar atmosphere exhibited no additional phases.

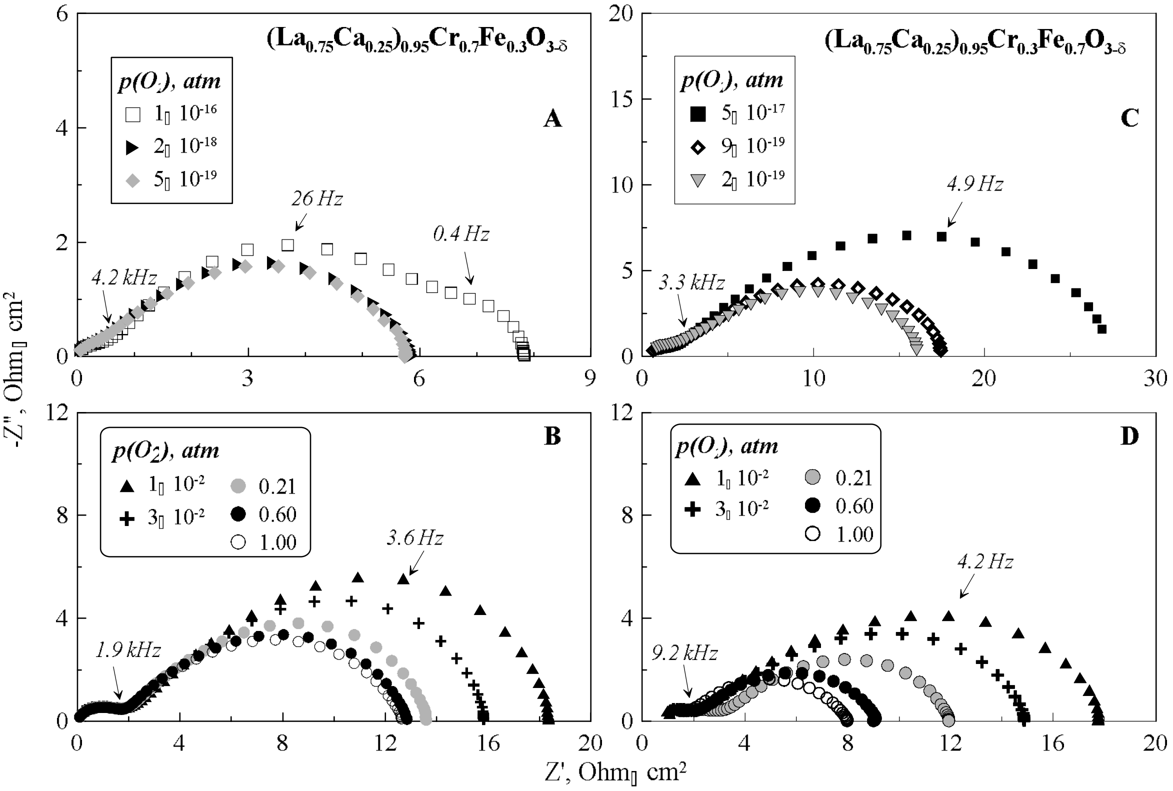



**Fig. 5.** Impedance spectra corrected for the electrode area and Ohmic resistance for $(La_{0.75}Ca_{0.25})_{0.95}Cr_{0.7}Fe_{0.3}O_{3-\delta}$ (A, B) and $(La_{0.75}Ca_{0.25})_{0.95}Cr_{0.3}Fe_{0.7}O_{3-\delta}$ (C, D) under reducing (A, C) and oxidizing (B, D) conditions.

According to Fig. 6, the activation energies of the electrode reactions both in reducing and oxidizing atmospheres are substantially higher for $(La_{0.75}Ca_{0.25})_{0.95}Cr_{0.3}Fe_{0.7}O_{3-\delta}$ as compared to the Cr-rich analogue regardless of the opposite trends in the conductivity behavior. This fact suggests that at least for one electrode composition the electrochemical activity is governed by factors independent of electron supply/removal to/from electrochemically-active sites. This suggestion is confirmed bysubstantially lower values of $E_a$ for the total conductivity (Fig. 3) than those for the electrochemical activity.The observed trends are not typical for most perovskite-based electrode [2, 7, 8] where the electronic conductivity is considered to be the major performance-determined factor, and might be attributed to differences in the microstructure or excessive formation of oxygen vacancies on the surface of Fe-enriched perovskiesleading to local ordering thathas the influence on the electro-catalytic properties. At the same time, the structural transition for $(La_{0.75}Ca_{0.25})_{0.95}Cr_{0.7}Fe_{0.3}O_{3-\delta}$ occurs at ~815 K, i.e. all the electrochemical tests were carried out on the material with rhombohedral or cubic structure. As for $(La_{0.75}Ca_{0.25})_{0.95}Cr_{0.3}Fe_{0.7}O_{3-\delta}$, the structural transformation occurred in the temperature rangewhere the electrochemical studies were carried out thatcould substantially affect its electrochemical behavior.

While decreasing hydrogen pressure over $(La_{0.75}Ca_{0.25})_{0.95}Cr_{0.7}Fe_{0.3}O_{3-\delta}$ anode leads to an appearance of additional low-frequency semicircle (Fig.5A) associated with retarded gas-phase diffusion, the $(La_{0.75}Ca_{0.25})_{0.95}Cr_{0.3}Fe_{0.7}O_{3-\delta}$ anode demonstrates a substantial enlargement of the intermediate-frequency arc (Fig. 4C) suggesting a higher role of surface-associated processes. Obviously, this phenomenon deserves further studies. One should remind that the increase of iron content in $(La_{0.75}Sr_{0.25})_{0.95}Cr_{1-x}Fe_xO_{3-\delta}$ also resulted in a deterioration of the electrochemical activity, presumably due to lower electronic conductivity [7]. Irrespective of the origin of such unexpected electrode behavior, the high level of the polarization resistance makes it necessary to modify the electrode composition, for instance, by fabrication of composite anodes, introduction of catalytically-active components or by a proper application of the current-collecting layer.

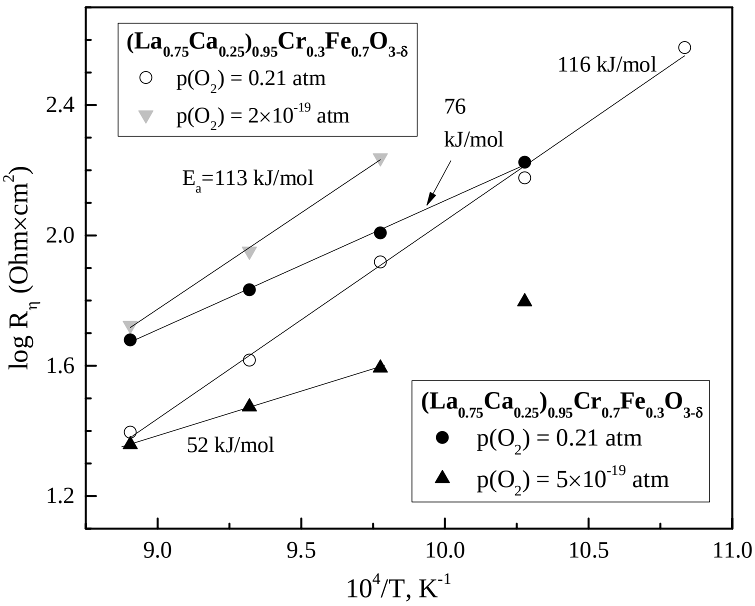



**Fig. 6.** Temperature dependencies of the polarization resistance of $(La_{0.75}Ca_{0.25})_{0.95}Cr_{1-x}Fe_xO_{3-\delta}$ electrodes in $O_2$ and wet 4% $H_2$-Ar atmospheres. The activation energies of the reciprocal total polarization resistance are marked near the corresponding data.

## Conclusions

Increasing iron content in $(La_{0.75}Sr_{0.25})_{0.95}Cr_{1-x}Fe_xO_{3-\delta}$perovskites leads to higher electronic conductivity, thermal expansion coefficient and electrochemical activity of the corresponding cathodes. Moreover, the temperature of the structural transition "orthorhombic" – "rhombohedral" shiftswith Fe-dopingtowards higher temperatures. The influence of Cr:Fe ratio under anode conditions is, however, different to that of the conductivity at low $p(O_2)$ indicating that other factors such as the structural transformation, anode microstructure or ordering of the surface oxygen vacancies,are responsible for the anode behavior. The high values of the polarization resistance require optimization of the electrode layers.

**Acknowledgements**

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### *BƏRK OKSİD YANACAQ ELEMENTLƏRİ ÜÇÜN ELEKTROD MATERİALLARI KİMİ $(La_{0.75}Ca_{0.25})_{0.95}Cr_{1-X}Fe_XO_{3-\Delta}$ PEROVSKİTLƏRIN İSTİFADƏ PERSPEKTİVİ*

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*Təqdim olunan iş bərk oksid yanacaq elementlərinin katod və anodları üçün istifadə oluna bilən $(La_{0.75}Ca_{0.25})_{0.95}Cr_{1-x}Fe_xO_{3-\delta}$ perovskitlərin sintezinə həsr olunub. Bu materiallar ortorombik struktura malikdilər, lakin 800-1000 K temperaturda qızdırdıqda romboedrik formaya keçirlər. Keçid temperaturu dəmirin miqdarından asılıdır. Xətti genişlənmə əmsalı $(10.5\text{-}11.1)\times10^{-6}K^{-1}$ intervalda dəyişir, həcmi dəyişiklər 0.16% təşkil edir.*

***Açar sözlər:** perovskit**,** termiki genişlənmə, faza keçidləri, xətti genişlənmə əmsalı**,** bərk oksid elementləri**.***

### *ПЕРОВСКИТОПОДОБНЫЕ $(La_{0.75}Ca_{0.25})_{0.95}Cr_{1-X}Fe_XO_{3-\Delta}$ ДЛЯ ПОТЕНЦИАЛЬНОГО ИСПОЛЬЗОВАНИЯ В КАЧЕСТВЕ ЭЛЕКТРОДНЫХ МАТЕРИАЛОВ СИММЕТРИЧНЫХ ТВЕРДООКСИДНЫХ ТОПЛИВНЫХ ЭЛЕМЕНТОВ*

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*Работа посвящена синтезу и аттестации перовскитов $(La_{0.75}Ca_{0.25})_{0.95}Cr_{1-x}Fe_xO_{3-\delta}$ в качестве потенциальных катодов и анодов твердооксидных топливных элементов (ТОТЭ). Для материалов характерна орторомбическая структура на воздухе, в то время как при нагреве свыше 800-1100 К происходит обратимый переход структуры в ромбоэдрическую симметрию. Температура перехода растет с содержанием железа. Значения линейного коэффициента термического расширения изменяются в интервале $(10.5\text{-}11.1)\times10^{-6}K^{-1}$, слегка увеличиваясь при легировании материалов железом, в то время как объемные изменения при восстановлении не превышают 0.16%. Электронная проводимость проявляет термически-активированный характер и увеличивается при введении железа, предположительно благодаря росту числа узлов* *доступных для электронного переноса. Данное поведение наблюдается в окислительных и восстановительных условиях. Низкий уровень электронной проводимости предположительно обуславливает недостаточно высокую каталитическую активность катодовна основе $(La_{0.75}Ca_{0.25})_{0.95}Cr_{1-x}Fe_xO_{3-\delta}$, в то время как в анодных условиях электрохимическое поведение связано с рядом других факторов, таких как электродная микроструктура или поверхностные явления.*

***Ключевые слова:*** *перовскит, фазовый переход, термическое расширение, химическое расширение, полная электропроводность, поляризационное сопротивление.*