

Available online at www.sciencedirect.com**ScienceDirect**

Procedia Engineering 98 (2014) 105 – 110

**Procedia
Engineering**www.elsevier.com/locate/procedia

11th International Symposium on Systems with Fast Ionic Transport, ISSFIT 11

Electrical and electrochemical properties of $\text{La}_2\text{NiO}_{4+\delta}$ -based cathodes in contact with $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$ electrolyte

E.Yu. Pikalova^{a,b,*}, N.M. Bogdanovich^a, A.A. Kolchugin^{a,c},
D.A. Osinkin^a, D.I. Bronin^{a,b}^a*Institute of High Temperature Electrochemistry, UB RAS, 20 Academicheskaya st., Yekaterinburg 620990, Russia*^b*Ural Federal University Named After the First President of Russia B.N. Yeltsin, 19 Mira st., Yekaterinburg 620002, Russia*^c*Vitus Bering Kamchatka State University, 4 Pogranichnaya st., Petropavlovsk Kamchatskiy 683032, Russia*

Abstract

The current work focuses on the investigation of the structural and electrical properties of $\text{La}_2\text{NiO}_{4\pm\delta}$, $\text{La}_{1.7}\text{Sr}_{0.3}\text{NiO}_{4\pm\delta}$ and $\text{La}_{1.7}\text{Ca}_{0.3}\text{NiO}_{4\pm\delta}$ layered perovskites and electrochemical performance of the cathodes on their base in contact with the $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ electrolyte with special attention given to the influence of the introduction of the sintering additives (CuO , $\text{Bi}_{0.75}\text{Y}_{0.25}\text{O}_{1.5}$) into cathode layers on their in-plane and polarization resistances. Studies by the dc four-probe technique and impedance spectroscopy were performed on the samples with/without the collector layer on a base of $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_3$ with different sintering temperatures of the electrode layers.

© 2014 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license

[\(http://creativecommons.org/licenses/by-nc-nd/3.0/\)](http://creativecommons.org/licenses/by-nc-nd/3.0/).

Peer-review under responsibility of the Gdansk University of Technology

Keywords: SOFC; cathode; Ruddlesden-Popper phase; layered perovskite; $\text{La}_2\text{NiO}_{4\pm\delta}$; in-plane resistance; polarization resistance

1. Introduction

Over the last decade, layered Ruddlesden-Popper phases with the generic formula $\text{A}_2\text{BO}_{4\pm\delta}$ (where A – a rare earth element or an alkaline earth element, or both, partially substituting one another; B – Cu, Ti, Cr, Mn, Fe, Co, Ni) have been studied as potential solid oxide fuel cell (SOFC) cathode materials [1-3]. The interest is based on their mixed ionic-electronic conductivity nature and good compatibility in the coefficient of thermal expansion (CTE)

* Corresponding author. Tel.: +7-343-362-33-94; fax: +7-343-374-59-92

E-mail address: e.pikalova@list.ru

with a wide row of solid state electrolytes, based on stabilized ZrO_2 , doped CeO_2 and LaGaO_3 . Among the materials investigated, $\text{La}_2\text{NiO}_{4+\delta}$ (LNO) was found to possess the highest value of the oxygen surface heteroexchange constant k , which is higher by one or two orders of magnitude than that for the best mixed conductors with perovskite structure, but its performance as a cathode is limited by its electronic conductivity [4]. The last mentioned can be increased, particularly, by appropriate doping on the A-site with Sr^{2+} or Ca^{2+} , what have been shown in some works, presented by different scientific groups [5-7]. Alternatively, the fabrication of functionally graded electrodes is being developed as a means to improve of their electrochemical activity [8,9]. The polarization resistance of an electrode can be improved by having a composition with high ionic conductivity as a functional layer, adjacent to the electrolyte, and grading to a composition with a higher value of electronic conductivity as a collector layer. In this work, both abovementioned strategies of the cathode performance improvement were applied to develop a cathode design for intermediate temperature SOFC. Compositions such as $\text{La}_2\text{NiO}_{4+\delta}$, $\text{La}_{1.7}\text{Sr}_{0.3}\text{NiO}_{4+\delta}$, $\text{La}_{1.7}\text{Ca}_{0.3}\text{NiO}_{4+\delta}$ were applied as a functional layer of bilayer electrodes in contact with the solid state electrolyte $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$. The composition with perovskite type structure $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_3$ with electronic conductivity in dependence on its porosity about 200-800 S/cm in temperature range 873-1073 K was used as a collector.

2. Experimental

The materials of the composition $\text{La}_2\text{NiO}_{4+\delta}$ (LNO), $\text{La}_{1.7}\text{Sr}_{0.3}\text{NiO}_{4+\delta}$ (LSNO), $\text{La}_{1.7}\text{Ca}_{0.3}\text{NiO}_{4+\delta}$ (LCNO) were synthesized via a two-step ceramic technology. The initial components La_2O_3 (LaO-D grade), NiO (pur.), CaCO_3 (pur.), SrCO_3 (pur.) were mixed in the required proportion and mixed in a planetary mill SAND in isopropyl alcohol media by steel balls for 1.2 h. After milling, the mixed powders were calcined at 1423 K for 2 h. The intermediate product underwent additional activation by milling in the planetary mill for 0.5 h followed by final synthesis at 1503 K for 5 h. After final sintering, powders were ball-milled until they had a specific surface area equal to 1 m^2/g for main part of experiments and 2.7 m^2/g for samples with low sintering temperature of functional layers (Brunauer-Emmett-Teller surface-area analysis (SORBI N.4.1 analyzer)). The surface morphology and chemical content of ceramic samples were characterized by scanning electron microscope JSM-5900LV (JEOL) equipped with EDS Inca Energy 250 spectrometer. To prepare the samples for electrical investigations the powders were pressed into the bars of 5×5×23 mm in size at 150 MPa and sintered at 1673 K for 5 h. To increase the samples' relative density sintering aid CuO was added in amount of 0.5 wt.%.

The electrolyte of $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (SDC) composition was synthesized via one-step ceramic technology, presented in details in [10], from CeO_2 (CeO-L grade) and Sm_2O_3 (SmO-L grade). After mixing, sintering at 1323 K for 2 h and ball-milling, the intermediate product was dry-pressed into disks at 150 MPa. The disks were then sintered at 1823 K for 3 h. According to XRD analysis (DMAX-2500, Rigaku Co. Ltd. diffractometer with Ni-filtered $\text{CuK}\alpha$ radiation in the range of $15^\circ \leq 2\theta \leq 85^\circ$), the specimens were single-phased and had the structure of cubic fluorite (Fm3m) with a unit cell parameter $a=5.5453(6)$ Å. The electrolyte specimens with relative density determined from the weight and the dimensions equal to 95–97% of the theoretical value had uniform grain distribution with little quantity of closed pores.

Additionally, $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_3$ (LNF), used in this work as a current collector layer, was synthesized by the Pechini method. Aqueous solutions of the starting materials $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (pur.), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (pur.) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (p.a) were mixed in a stoichiometric cation ratio. After organic fuels such as citric acid and ethylene glycol were added, the mixed solution was heated at approximately 723 K until self-ignition. The obtained precursor was calcined at 1173 K for 6 h in air and ball-milled. The XRD pattern of calcined powder could be indexed as a single phase rhombohedrally distorted perovskite structure with unit cell parameters $a=5.5053(4)$ Å and $c=13.2727(9)$ Å. After the heat treatment the specific surface area of powder was about 6.5 m^2/g .

Conductivity of compact samples (approximately 12×4.5×2.5 mm) of different compositions was measured by a direct current four-probe method in air. Current and voltage probes on samples were made from platinum wire 0.1 mm in diameter. The measurements were performed in the temperature range of 673-1073 K with steps of 50 degrees with isothermal exposure 1 h within it. The temperature of the measuring cell for 5 samples was controlled with a TP-403 thermal regulator (VARTA) within an accuracy of 1 degree.

For electrochemical characterization the electrodes were fabricated symmetrically on the 1 mm thick SDC electrolyte substrates with area of 0.25-0.36 cm^2 in the form of two-layer coatings with functional and collector layers (Fig. 1). The cathode slurries were prepared by mixing the powdered components with ethyl alcohol and polyvinylbutyral binder in the planetary mill. The functional cathode layers were placed onto a substrate by painting

several times followed by sintering at 1473-1673 K. The estimated thickness of functional layers was approximately 30-40 μm . The LNF collector layer was sited onto the pre-sintered functional layers. The sintering temperature of the collector layer was 1473-1523 K and in all cases did not exceed the functional layer sintering temperature and its thickness varied from 30 (for impedance investigations) to about 100 μm (for in-plane resistance study). The estimated porosity of electrode layers was about 45 %. In a row of LCNO samples the additives such as 2 wt. % CuO and 5 wt.% $\text{Bi}_{0.75}\text{Y}_{0.25}\text{O}_{1.5}$ (YDB) were introduced which enabled the sintering temperature to be reduced.

The electrochemical measurements were carried out by the method of impedance spectroscopy using a frequency response analyzer FRA-1260 with the electrochemical interface EI-1287 (Solartron Instruments Inc.) in the frequency range of 0.005-0.1 Hz to 100 kHz at the amplitude of applied sinusoidal signal of 10-20 mV. The electrochemical cell was connected to an impedance meter via a two-electrode four-cable mode which permits the exclusion of the impedance of current-supplying cables from the overall impedance of the system. The polarization resistance (R_{η}) of electrochemical cell with symmetrically arranged electrodes was calculated as following:

$$R_{\eta} = \frac{(R_{dc} - R_{hf})S}{2}, \quad (1)$$

where S is the surface area of electrode, R_{dc} is the dc resistance of electrochemical cell, and R_{hf} is the resistance determined by extrapolation of the high-frequency part of an impedance spectrum up to a crossing with x-axis and, in most cases, related to the electrolyte resistance, contact electrolyte-electrode resistance and a part of lateral resistance of the electrode.

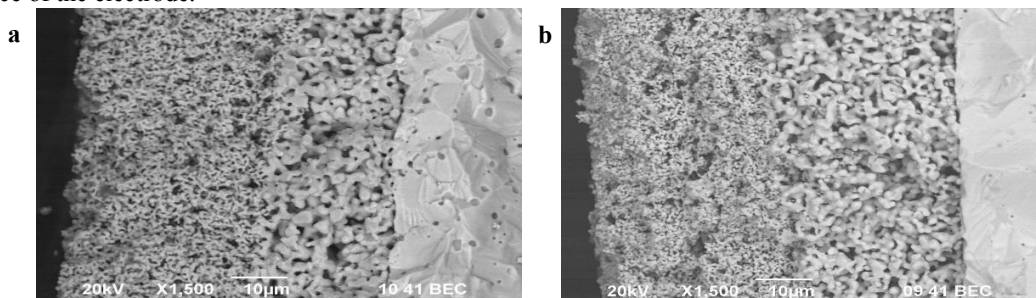


Fig. 1. The microstructure of the bilayer electrodes on the SDC electrolyte substrate: (a) LNF (collector layer, $T_s=1523$ K) – LSNO (functional layer, $T_s=1573$ K) – SDC; (b) LNF (collector layer, $T_s=1523$ K) – LCNO (functional layer, $T_s=1523$ K) - SDC.

3. Results and discussion

3.1. Crystal structure

The results of X-ray diffraction analysis reveal for all the samples appearance of tetragonal structure (14/mmm space group). The phase identification was performed by using JCPDS card file and software package Peak Find v1.03. The lattice parameters were calculated by Rietveld method. The decrease in a parameter (Table 1) both in case of doping Sr^{2+} and Ca^{2+} can be explained in terms of the changes in nickel oxidation state from +2 to +3 as a result of charge compensation and in the size of nickel cations from larger Ni^{2+} (0.69 Å) to smaller Ni^{3+} (0.60 Å). In some works [11, 12] was shown that the trivalent nickel created by substitution is in the low-spin state ($t_{2g}^6 e_g^1$). The changes in c parameter are defined by the dimensional factor due to the substitution of La^{3+} (1.21 Å) by a larger cation Sr^{2+} (1.27 Å) and a smaller cation Ca^{2+} (1.18 Å).

Table 1. Lattice parameters of tetragonal structure dependent on the composition of samples

Samples composition	a (Å)	c(Å)
$\text{La}_2\text{NiO}_{4+\delta}$	3.8702(4)	12.6973(15)
$\text{La}_{1.7}\text{Sr}_{0.3}\text{NiO}_{4+\delta}$	3.8367(4)	12.7111(15)
$\text{La}_{1.7}\text{Ca}_{0.3}\text{NiO}_{4+\delta}$	3.8350(3)	12.6141(12)

Another factor should be taken into account: during preparation of layered perovskites small amount of excess oxygen is taken up from the oxygen atmosphere, which is present in the tetrahedral interstitial sites between the (La (Sr,Ca)O) rock-salt layers. Comparison of the lattice parameters received with those presented in literature reveals that the preparation method chosen in this work studied substances with high δ values. For example, the determination of oxygen content in LCNO by wet chemical methods and its c -axis values, presented in [13] $c=12.607(2)$ for $\delta=0.03$ (preparation in oxygen atmosphere) and $c = 12.596(2)$ for $\delta=0.01$ (preparation in argon atmosphere), while in this work $c=12.6141(12)$. A higher degree of compressive stress in the Ni–O bonds in LCNO at the same doping level compared with that in LSNO would be anticipated to keep the oxygen content higher in LCNO. Nevertheless, it is known, that the content of the over-stoichiometric oxygen both in LSNO and LCNO decreases remarkably relative to LNO [6].

3.2. Electrical and electrochemical properties of LNO, LSNO and LCNO-based cathodes

Fig. 2 a presents the temperature dependences of the electrical conductivity of the compact samples. As would be expected, the conductivity of LNO increases with doping and is the highest in the case of doping with Ca. In addition, the conductivity values are strongly affected by the relative density of samples, and its increase from 82-83 % to 87-88% at sintering with copper oxide results in conductivity grows by 15-20 %. However the conductivity even of doped samples does not exceed 100 S/cm and the usage such materials in cathodes without a current collector layer is problematic.

$\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_3$ (LNF) with high value of electronic conductivity (Fig. 2 b) has been used in this study as a current collector layer in bilayer electrodes. With decreasing of relative density the conductivity of LNF sharply decreases, nevertheless for the sample with porosity about 50% the conductivity value is about 200 S/cm, what is suitable for its usage as a collector. How it was mentioned in experimental description, the sintering temperature of the collector layer did not exceed the sintering temperature of the functional layer that kept the microstructure of the last close to initial state. The application of LNF as the second layer does not lead to significant thermo-mechanical stresses, because its CTE value ($12.4 \times 10^{-6} \text{ K}^{-1}$) is close to CTE's of LNO-based materials ($12.7\text{-}13.5 \times 10^{-6} \text{ K}^{-1}$).

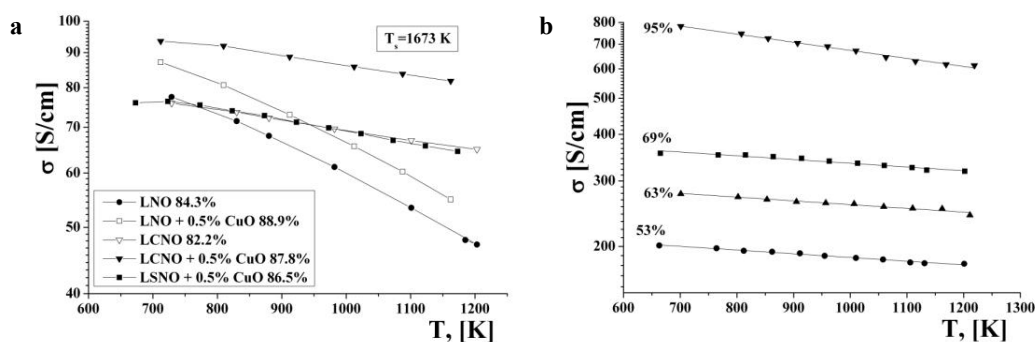


Fig. 2. The temperature dependence of (a) electrical conductivity of compact samples of LNO, LCNO and LSNO with/without CuO additive and (b) electrical conductivity of LNF with different relative density.

It is clearly seen, that the application of the collector layer strongly influences the electrochemical activity of the electrodes (Fig. 3 a), while sintering temperature shows insignificant effect. However it worth noting, that at the sintering temperature 1473 K adhesion of electrodes to electrolyte was poor and only at 1573 K became quite sufficient.

Temperature dependences of the polarization resistance of bilayer electrodes with functional LNO, LCNO and LSNO layers sintered at 1573 K are presented in Fig. 3 b. Evidently, the electrochemical activity of undoped LNO is maximal. The most probable reason for higher polarization resistance of electrodes with LCNO and LSNO functional layers, how was proposed before, is a lower content of over-stoichiometric oxygen, which in layered perovskites is the main participant in oxygen transport [14]. In the last part of the work the LCNO-LNF bilayer electrode has been chosen for the further studies in spite of its higher polarization resistance by comparison with the LNO-LNF electrode. Some reason for that is the lower electrical resistivity of the LCNO and lower interaction with SDC as compared with LNO [15].

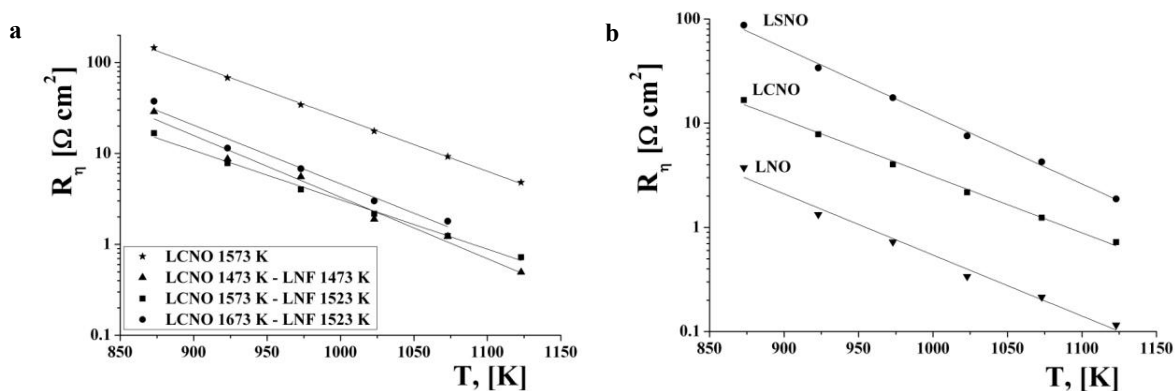


Fig. 3. Polarization resistance of a) LCNO cathode, sintered at different temperature and with/without LNF collector, b) LNO, LSNO and LCNO cathodes, sintered at 1573 K, with LNF collector sintered at 1523 K.

3.3 Influence of sintering aids on the properties of LCNO-LNF bilayer cathodes

For the better current distribution in electrochemical devices the in-plane resistance of the electrodes should be reduced to as low value as possible. It may be achieved by introducing some sintering additives into the materials of the functional and/or collector layer. Such a modification may on the one hand result in lowering the sintering temperature of the electrode layers and, on the other hand, change electrochemical activity of the electrodes [10, 16].

Chosen as a sintering aids, CuO in amount 2 wt. % (specific surface $10.3 \text{ m}^2/\text{g}$ in functional layer and $3.2 \text{ m}^2/\text{g}$ in collector layer) and YDB in amount 5 wt.% (only in collector layer with $1.2 \text{ m}^2/\text{g}$) were introduced into electrode slurries during stirring. CuO additive promotes decrease in sintering temperature of the electrode layers by 200-400 degrees with its good adhesion to each other and to the electrolyte. Fig. 4 a shows in-plane resistance of such modified cathodes. For the purpose of comparison data for LCNO sintered at different temperatures without collector layer and LCNO with CuO additive without collector layer are also given.

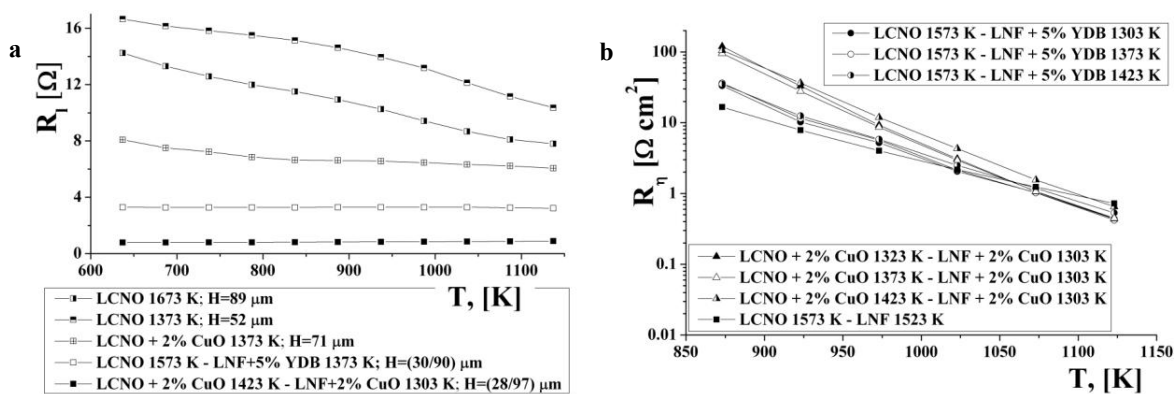


Fig. 4. In-plane (a) and polarization (b) resistance of LCNO cathode, modified with CuO and YDB.

As is seen, the additives decreased the in-plane resistance of the electrode layers. The CuO is more effective additive than YDB. Fine copper oxide powder is well dispersed and forms a liquid phase and a solid solution with all the components of the electrode and surface layer of the electrolyte that leads both to an improvement and expansion of contact with the solid electrolyte substrate and between the grains of the high-porous electrode structure. YDB additive also considerably decreases the in-plane electrode resistance and besides facilitates oxygen exchange at low temperatures decreasing polarization resistance of electrodes in comparison with Cu-containing electrodes (Fig. 4 b). Short-term tests during 370 hours have demonstrated that the electrode activity of LCNO electrode with 2% CuO sintered at 1373 K increases with time and its polarization resistance changes from 0.40 to $0.34 \Omega \text{ cm}^2$ at 1123 K. In the same test the electrodes both with YBD and without additives were prone to ageing increasing R_p from 0.84 to $1.34 \Omega \text{ cm}^2$ and from 0.52 to $2.23 \Omega \text{ cm}^2$, respectively.

Conclusions

Layered oxide compositions LNO, LCNO and LSNO were synthesized and tested individually and in contact with solid state electrolyte SDC and was found that in spite of electrical conductivity increasing the doping leads to a significant worsening of polarization resistance (0.12, 0.72 and 1.88 Ω cm² at 1123 K, respectively), which may be connected with a decrease in over-stoichiometric oxygen content with doping, especially by Sr²⁺. It was found that decreasing sintering temperature up to 1373 K, particularly by means of introduction of sintering aids, such as CuO and YBD, and applying high conducting LNF as a collector layer enable to fabricate the cathodes on the base of LCNO with good adhesion and electrochemical activity. The bilayer LCNO-LNF electrode with 2 wt. % CuO both in functional and collector layers demonstrates stability of electrode characteristics in time with small decreasing of polarisation resistance from 0.40 to 0.34 Ω cm² at 1123 K. However, sintering aids investigated do not improve electrochemical properties of doped electrodes in comparison with LNO and future work will be aimed at further improvement of their characteristics by different methods.

Acknowledgements

This work has been partly done using facilities of the shared access center "Composition of compounds" IHTE, UB RAS, and supported by the Russian Foundation for Basic Research, the Government of Sverdlovsk region and Presidium of Ural Branch of RAS (projects №№13-03-96098, 14-03-00414, 14-08-31030, 12-S-3-1016).

References

- [1] E. Boehm, J.-M. Bassat, P. Dordor, F. Mauvy, J.C. Grenier, Ph. Stevens, Oxygen diffusion and transport properties in non-stoichiometric Ln_{2-x}NiO_{4+δ} oxides, *Solid State Ionics* 176 (2005) 2717-2725.
- [2] W.D. Pérez-Coll, A. Aguadero, M.J. Escudero, P. Núñez, L. Daza, Optimization of the interface polarization of the La₂NiO₄-based cathode working with the Ce_{1-x}Sm_xO_{2-δ} electrolyte system, *J. Power Sources* 178 (2008) 151-162.
- [3] M. Greenblatt, Ruddlesden-Popper Ln_{n+1}Ni_nO_{3n+1} nickelates: structure and properties, *Current Opinion in Solid State and Mat. Sci.* 2 (1997) 174-183.
- [3] R.J. Woolley, S.J. Skinner, Functionally graded composite La₂NiO_{4+δ} and La₄Ni₃O_{10-δ} solid oxide fuel cell cathodes, *Solid State Ionics* 255 (2014) 1-5.
- [4] C. Lalanne Synthèse et mise en forme de nouveaux matériaux de cathode pour piles ITSOFC: réalisation et tests de cellules. L'université Bordeaux 1, Ecole Doctorale des Sciences Chimiques, France, 2005.
- [5] K. Ruck, G. Krabbes, I. Vogel, Structural and electrical properties of La_{2-x}Ca_xNiO_{4+δ} (0 < x < 0.4) with regard to the oxygen content, *Mater. Res. Bull.* 34 (1999) 1689-1697.
- [6] J.P. Tang, R.I. Dass, A. Manthiram, Comparison of the crystal chemistry and electrical properties of La_{2-x}A_xNiO₄ (A = Ca, Sr and Ba), *Mater. Res. Bull.* 35 (2000) 411-424.
- [7] S.P. Tolochko, L.V. Makhnach, I.F. Kononyuk, V.V. Vashuk, V.A. Lomonosov, J. Hauck, H. Altenburg, V.M. Shelekhina, Preparation of La_{2-x}Sr_xNiO₄ (x = 0-1.3) conducting oxides via a citrate route, *Inorg. Mat.* 36 (2000) 1137-1140.
- [8] C. Setevich, F. Prado, D.Z. de Florio, Effects of the electrode configuration, phase relationship and microstructure on the polarization resistance of La_{0.3}Ba_{0.7}CoO_{3-δ} as cathode material for T-SOFC, *Int. J. Hydr. Energy* 37 (2014) 8738-8743.
- [9] R.J. Woolley, S.J. Skinner, Functionally graded composite La₂NiO_{4+δ} and La₄Ni₃O_{10-δ} solid oxide fuel cell cathodes, *Solid State Ionics* 255 (2014) 1-5.
- [10] N. Bogdanovich, V. Gorelov, V. Balakireva, T. Dem'yanenko, Effect of Copper on Solid Electrolytes (Ce_{0.8}Sm_{0.2})_{1-x}Cu_xO_{2-δ} and Composite Cathodes Based on La_{0.8}Sr_{0.2}MnO₃, *Russ. J. Electrochem.*, 41(2005) 576-581.
- [11] J. Gopalakrishnan, G. Colmann, B. Reuter, Studies on the La_{2-x}Sr_xNiO₄ (0≤x≤1) system, *J. Solid State Chem.* 22 (1977) 145-149.
- [12] V.P. Fedorchenko, G.V. Loshkarev, A.V. Zyrin, E.A. Matveenko, E.I. Malkin, Magnetic properties of the solid state solutions of lanthanum nickelates doped with calcium, *Materialy Elektronnoi Tekhniki (Materials of Electronic Technics)* 1 (2007) 49-52, in russian
- [13] K. Ruck, M. Ruck, G. Krabbes, Structural properties of La_{1.7}Ca_{0.3}NiO₄, *Mater. Res. Bull.* 34 (1999) 933-938.
- [14] L. Minervini, R.W. Grimes, J. Kilner, K.E. Sickafus, Oxygen migration La₂NiO_{4+δ}, *J. Mat. Chem.* 10 (2000) 2349-2354.
- [15] E.Yu. Pikalova, A.A. Kolchugin, N.M. Bogdanovich, D.I. Bronin, Electrical and Electrochemical Properties of La_{2-x}Ca_xNiO_{4+δ} and La_{2-x}Ca_xNiO_{4+δ}-Ce_{0.8}Sm_{0.2}O_{1.9} Cathode Materials for Intermediate Temperature SOFCs, submitted in Techna Group series "Advances in Science and Technology" 87 (2014)
- [16] N.M. Bogdanovich, D.I. Bronin, G.K. Vdovin, I.Yu. Yaroslavtsev, B.L. Kuzin, Effect of Bi_{0.75}Y_{0.25}O_{1.5} electrolyte additive in collector layer to properties of bilayer composite cathodes of solid oxide fuel cells based on La(Sr)MnO₃ and La(Sr)Fe(Co)O₃ compound, *Russ. J. Electrochem.* 45 (2009) 456-464.