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SEMICONDUCTOR PHYSICS INSTITUTE

Tomas Šalkus

INVESTIGATION OF THE CORRELATION BETWEEN STRUCTURE, ELEMENTAL COMPOSITION, AND CHARGE CARRIERS' TRANSPORT IN Li^{+}, V$_{O}^{\bullet\bullet}$ SOLID ELECTROLYTES

Summary of doctoral dissertation

Technological Sciences, Material Engineering (08 T)

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PUSLAIDININKIŲ FIZIKOS INSTITUTAS

Tomas Šalkus

Li^+, $V_O^{\bullet\bullet}$ SUPERJONIKŲ STRUKTŪROS, ELEMENTINĖS SUDĖTIES IR KRŪVININKŲ PERNAŠOS SĄSAJŲ TYRIMAS

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Introduction

Motivation of the dissertation. Li^+ ion and oxygen vacancy ($V_O^{\bullet\bullet}$) solid electrolytes (SE) were fabricated and investigated in this work. Lithium-ion SE can be used in all-solid-state lithium batteries or CO_2 gas sensors. In order to increase the efficiency of these devices new SE with possibly higher ionic conductivity and lower their activation energy are in quest. One way to achieve this objective is to modify $LiM_2^{IV}(PO_4)_3$ or $Li_3M_2^{III}(PO_4)_3$-type lithium SE fully or partially substituting three valence M^{III} or four valence M^{IV} element by other elements. Thus the quantity and mobility of mobile lithium ions is changed in the material. Unfortunately, the advance prediction of ionic conductivity and its activation energy of a new compound is practically impossible, therefore one of the aims of this thesis was the search for new lithium SE. To reach this aim new SE were made, these were $Li_3Ce_2(PO_4)_3$ (can also be written as $LiCe_{2/3}PO_4$), $LiCe_2(PO_4)_3$ (otherwise $Li_{1/3}Ce_{2/3}PO_4$), $Li_3Sc_{0.3}Ce_{1.7}(PO_4)_3$, $Li_3Sc_{2-x}B_x(PO_4)_3$ (where $x = 0-2$), $Li_{1+x}Ge_{2-2x}Ti_xAl_x(PO_4)_3$, $Li_{1+x}Zr_{2-2x}Ti_xAl_x(PO_4)_3$, $Li_{1+x}Sc_xZr_{2-x}(PO_4)_3$ (where $x = 0.1$, 0.2, 0.3), $Li_{2.9}Sc_{1.8}Y_{0.1}Zr_{0.1}(PO_4)_3$, $Li_{2.8}Sc_{1.7}Y_{0.1}Zr_{0.2}(PO_4)_3$, $Li_{2.9}Sc_{1.9}Zr_{0.1}(PO_4)_3$. High values of conductivity of $Li_{1.3}La_{0.3}Ti_{1.7}(PO_4)_3$ and $Li_{3x}La_{2/3-x}TiO_3$ ($x = 0.11$) compounds stimulated their further investigation in high electrical field's frequency range.

$V_O^{\bullet\bullet}$ SE are used in solid oxide fuel cells (SOFC). Usually SOFC consist of four functional parts: anode, SE membrane, cathode, and interconnect. SOFC ceramic membrane should have the following features: high density, low electronic conductivity component, and possibly higher conductivity caused by oxygen vacancies' transport. ZrO_2-8 mol% Y_2O_3 (yttria stabilized zirconia – YSZ) $V_O^{\bullet\bullet}$ SE meets these criteria the best. In order to reduce the working temperature of SOFC to 900 K the thickness of the membrane should be reduced. ZrO_2-8 mol% Y_2O_3 films with thicknesses in the range of micrometer were made by magnetron sputtering and their ionic conductivities were investigated in this work. The function of the anode (fuel electrode) is completely different – the oxidation of the fuel should proceed effectively in SOFC anodes. They should be porous in order fuel (methane, hydrogen gases) could reach reaction sites easily, good ionic and electronic conductors. To make SOFC anode with lower

polarisation resistance Ni-CGO composite films were prepared by spray pyrolysis. Electrical properties of the films were investigated after different their temperature treatments. The dimensions of the crystallites can be varied in the range from several to some hundred nanometres using this method. There is little information about technological conditions of producing Ni-CGO films with grains in the nanometre range and their electrical properties were not studied yet. $La_{1-x}Sr_xCo_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF) materials are usually used as SOFC cathodes.

Electrical properties of SE were investigated by impedance spectroscopy (IS) method in the electrical field frequencies from 1 to 10^9 Hz. The crystal structure of the samples were determined by X-ray diffraction (XRD) method, temperature analysis (differential thermal analysis – DTA, differential scanning calorimetry – DSC, thermogravimetric analysis – TGA) of the samples was also done. The surfaces of the sintered ceramics were investigated by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and X-ray photoelectron spectroscopy (XPS). Various investigation methods used in this work enables one to determine the influence of elemental composition and technological conditions of preparation of SE on their electrical properties.

The main **aim** of the dissertation was to find out correlation between structure, elemental composition, and electrical properties in Li^+ conducting ceramics and $V_O^{\bullet\bullet}$ conducting films. To seek the aim the following **problems** were solved:

1. New Li^+ conducting ceramics changing stoichiometric parameters x and y in the systems $Li_{1+x}Ge_{2-2x}Ti_xAl_x(PO_4)_3$, $Li_{1+x}Zr_{2-2x}Ti_xAl_x(PO_4)_3$, $Li_3Sc_xCe_{2-x}(PO_4)_3$, $Li_{1+x}Sc_xZr_{2-x}(PO_4)_3$, $Li_3Sc_{2-x}B_x(PO_4)_3$, and $Li_{3-x}Sc_{2-x-y}Y_yZr_x(PO_4)_3$ have been sintered under different technological conditions (sintering duration and temperature).

2. Microstructure, temperature stability, and electrical properties in broad electrical field's frequency range and temperature range of the above mentioned ceramics have been investigated.

3. Ni-CGO films with different microstructure have been fabricated by spray pyrolysis and their electrical properties were investigated.

4. The influence of technological conditions of fabrication of YSZ thick films by magnetron sputtering on their electrical properties have been investigated.

Novelty of the thesis.

1. Optimal technological conditions of fabrication of Li^+-conducting ceramics have been found.

2. New experiment was performed in order to establish the type of conduction in monazite-type structure $LiCe_{2/3}PO_4$ – the change of Li^+ concentration on the surface of the ceramics has been measured by XPS after heating the sample in electrical field.

3. The influence of stoichiometric factors and ceramic's microstructure of the above mentioned Li^+ SE on their bulk and grain boundary conductivities and temperature of phase transition has been investigated for the first time.

4. The influence of the microstructure of Ni-CGO films on their polarization resistance has been investigated for the first time.

Statements presented for defence.

1. Ionic conductivity of SE compound increases after partial substitutions $Zr^{4+} \rightarrow Sc^{3+} + Li^+$ or $2Zr^{4+} \rightarrow Al^{3+} + Li^+ + Ti^{4+}$ in $LiZr_2(PO_4)_3$, and after partial substitution $Ce^{3+} \rightarrow Sc^{3+}$ in $Li_3Ce_2(PO_4)_3$.

2. Phase transition temperature in $Li_3Sc_{2-x}B_x(PO_4)_3$ and $Li_{3-x}Sc_{2-x-y}Y_yZr_x(PO_4)_3$ systems is changed by changing stoichiometric factors x and y.

3. Technological conditions of fabrication of Ni-CGO films influence the microstructure and polarization resistance of SOFC anode.

Practical importance of the thesis. Li^+ SE investigated in this work can be used for CO_2 gas sensors or solid state Li^+ batteries. $V_O^{\bullet\bullet}$ conductors can be used for SOFC. The results of the investigation can be used for choosing optimal conditions for their fabrication.

Outline of the thesis

The dissertation consists of an introduction, three chapters, conclusions, and a list of references.

The motivation of the performed investigation, the aim of the dissertation, solved problems, the novelty of the results, statements presented for defence, and practical importance of the thesis are presented in **Introduction**.

Chapter 1 is literature review. Crystal structures and electrical properties of NASICON-type $LiM_2^{IV}(PO_4)_3$, $Li_3M_2^{III}(PO_4)_3$ (where M^{IV} is four valence element and M^{III} is three valence element) [1-3] and perovskite type $Li_{3x}La_{2/3-x}TiO_3$ SE [4] are presented. The changes of the structure, lithium distribution in the $[M_2(PO_4)_3]^{3-}_{3\infty}$ framework [5, 6], and increase of ionic conductivity [7] during superionic phase transitions in NASICON-type materials are shown. The influence of the substitutions of element M in these SE on their ionic conductivity is analysed. For example a partial substitution $Ti^{4+} \rightarrow M^{III}$ (where $M^{III} = Al^{3+}$, Sc^{3+}, Y^{3+}, Fe^{3+}, La^{3+}, Cr^{3+}, Ga^{3+}, In^{3+}) increases ionic conductivity by several orders of magnitude [8, 9].

The structures of $V_O^{\bullet\bullet}$ conductors ZrO_2 and CeO_2 stabilized by other oxides are discussed. The influence of additives in zirconias and cerias on $V_O^{\bullet\bullet}$ conductivity is shown. The addition of several mol% CaO, Y_2O_3 or Sc_2O_3 into ZrO_2 increases the vacancy concentration in the material as well as $V_O^{\bullet\bullet}$ conductivity [10-11]. The addition of Gd_2O_3 or Sm_2O_3 into CeO_2 is commonly used to increase the ionic conductivity of the material [12, 13].

Experimental methods used in this work are described in **chapter 2**. All Li^+ SE were synthesized by solid state reaction. The method is based on milling and heating of the initial stoichiometric mixtures of CeO_2, Li_2CO_3, $NH_4H_2PO_4$, Sc_2O_3, H_3BO_3, La_2O_3, TiO_2, ZrO_2, GeO_2, $Al_2O_3 \cdot 2.5H_2O$, Y_2O_3 in ethyl alcohol for several times. Ceramic pellets have been pressed and sintered from obtained SE powders choosing different sintering durations and temperatures.

Amorphous NiO-CGO films were obtained by spray pyrolysis from $Ni(NO_3)_2 \cdot 6H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$, and $GdCl_3 \cdot 6H_2O$ solutions in 10:90 vol% ethanol and tetraethylenglycol. A mask was used for spraying the films on CGO or YSZ thick ceramic substrates. Annealing temperatures from 920 to 1470 K have been chosen for crystallization of the films and the crystallite sizes in the films from 2 nm to 260 nm have been obtained. NiO has been reduced to metallic Ni in H_2 atmosphere.

Several experimental SOFCs have been created to test electrochemical performance of Ni-CGO anodes. Pt layer has been sputtered on top of the anode of SOFC, Pt mesh, Pt paste, and Pt wires have been used to form current collectors. Only Pt layer has been

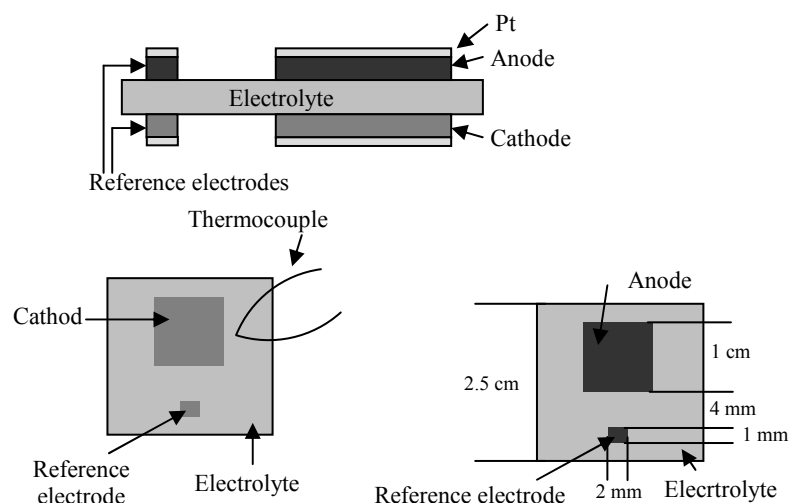used for cathode or symmetrical cells with Ni-CGO on both sides of the substrate have been made.

Fig. 1. Schematic view of cells for electrochemical characterization.

For sputtering of ZrO_2-8 mol% Y_2O_3 films DC magnetron has been connected to $2 \cdot 10^3$ Hz $307 \div 360$ V voltage and $1 \div 1.5$ A current generator. Ni-cermet and alloy-600 have been used as substrates. The films were sputtered varying sputtering duration from 0.5 to 10 h, using 0 or 100 V offset voltage and changing O_2 gas pressure from 0.5 to 1.8 Pa.

DRON 3 M, PHILIPS X-Spert, and BRUCKER D8 Advance spectrometers were used for XRD analysis. Netzsch STA 449 C, TA Instruments SDT Q600, and SETARAM DSC111 were used for thermal analysis of the powders. Carl Zeiss SMT AG EVO 50EP and Carl Zeiss Leo 1530 SEMs were used for surface analysis of the ceramics.

XPS experiments were performed by RIBER LAS-3000 spectrometer. Elemental composition on the surfaces of the ceramics has been obtained from XPS spectra. In order to establish conduction type of $Li_3Ce_2(PO_4)_3$ ceramics a special experiment has been performed. Platinum electrodes have been prepared on $LiCe_{2/3}PO_4$ ceramic cylindrical sample ($\varnothing$ 8 mm, 1 mm thick) by applying a conductive Pt paste. The first electrode covered the bottom surface of the pellet and the second electrode had a shape of a ring and was placed on the top surface and was connected to the negative potential (Fig. 2). The ceramic sample was placed in XPS chamber and evacuated. Then external permanent electric field (E) was applied to the sample and it was heated at the

temperature 493 K for 1 h. Then the sample under electric field was cooled down to room temperature. The surface of the sample which was under negative electrode was studied by XPS without external permanent electric field.
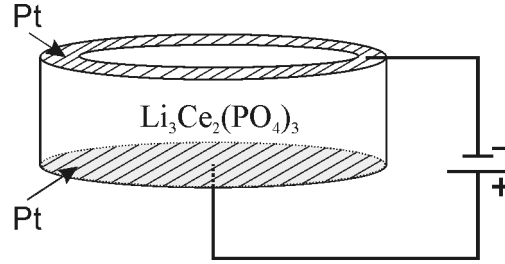

Fig. 2. Specially prepared $Li_3Ce_2(PO_4)_3$ sample for XPS study of the influence of E on the concentration of Li^+ ions on the surface.

Special attention has been devoted to IS method. Electrical impedance $\widetilde{Z}(f) = Z' - iZ''$ is usually represented in complex plain plot, where two semicircles with centres below real axis are observed for the SE ceramic samples. The semicircle in $Z''(Z')$ plot at higher frequencies corresponds to bulk resistance (Z_b) and the one at lower frequencies corresponds to resistance of grain boundaries of the ceramic (Z_{gb}). Measurements of impedance covered frequency range from 1 Hz to 1 GHz and temperature range $300 - 600$ K of lithium-conducting ceramics. At the lower frequency range ($1 - 10^6$ Hz) Solartron 1260 and Shchlumberger 1255 frequency response analysers were used for two electrode measurements and self-made equipment was used to measure impedance by four electrode method [14]. Coaxial line spectrometer with a sample inserted in the inner conductor was used for the measurements of transmission coefficient ($\widetilde{T}$) in the frequencies from 10^6 Hz to 10^9 Hz. $\widetilde{Z}(f)$ were calculated from $\widetilde{T}$ [15, 16]. Specific impedance of the ceramic is

$$\widetilde{\rho} = \widetilde{Z}\frac{S}{l},\tag{1}$$

where: S – surface area of the electrode, l – sample length and complex conductivity

$$\widetilde{\sigma} = \sigma' + i\sigma'' = \frac{1}{\widetilde{\rho}}.\tag{2}$$

Pt or carbon electrodes were used to contact Li^+ samples.

HP Precision LCR Meter 4284A was used to study frequency dependences of impedance YSZ films. Impedances of SOFC with Ni-CGO anodes were measured at

temperatures from 723 K to 873 K by Zahner IM6 and Solartron SI1260 + SI1287 impedance meters. Two and three electrode methods were used for SOFC study in the frequency range $10^{-1} - 10^5$ Hz in H_2:N_2 atmosphere.

The experimental results are presented in **chapter 3**. XRD analysis of the Li^+-conducting compounds has shown, what $Li_{1/3}Ce_{2/3}PO_4$, $LiCe_{2/3}PO_4$, $Li_3Sc_{0.3}Ce_{1.7}(PO_4)_3$, $Li_3Sc_{2-x}B_x(PO_4)_3$ (where x = 0–2), $Li_{2.9}Sc_{1.9}Zr_{0.1}(PO_4)_3$, and $Li_{2.9}Sc_{1.8}Y_{0.1}Zr_{0.1}(PO_4)_3$ compounds belong to monoclinic symmetry (space group P2$_1$/n) with $Z = 4$ formula units in the lattice. $Li_{2.8}Sc_{1.8}Zr_{0.2}(PO_4)_3$ and $Li_{2.8}Sc_{1.7}Y_{0.1}Zr_{0.2}(PO_4)_3$ compounds belong to orthorhombic symmetry (s.g. Pbcn), $Z = 4$. $Li_{1.1}Sc_{0.1}Zr_{1.9}(PO_4)_3$, $Li_{1.2}Sc_{0.2}Zr_{1.8}(PO_4)_3$, $Li_{1.3}Sc_{0.3}Zr_{1.7}(PO_4)_3$, $Li_{1+x}Zr_{2-2x}Ti_xAl_x(PO_4)_3$, and $Li_{1+x}Ge_{2-2x}Ti_xAl_x(PO_4)_3$ (where x = 0.1, 0.2, 0.3) compounds belong to rhombohedral symmetry (s.g. R$\overline{3}$c), $Z = 6$. The above mentioned compounds have typical NASICON-type structure.

DTA curves of $Li_{2.9}Sc_{1.9}Zr_{0.1}(PO_4)_3$ and $Li_{2.9}Sc_{1.8}Y_{0.1}Zr_{0.1}(PO_4)_3$ SE powders are presented in Fig. 3.
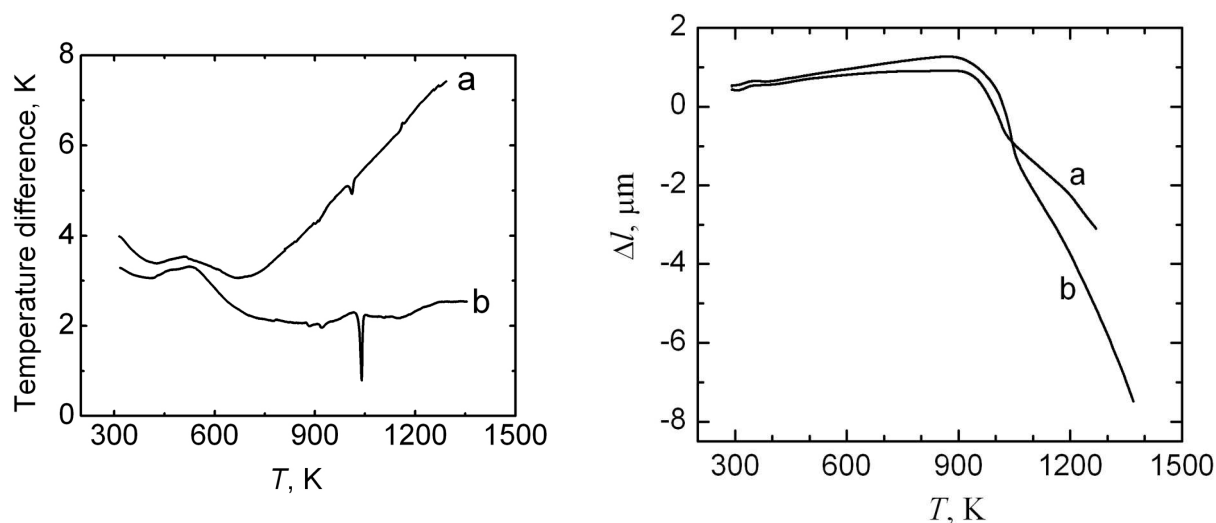

Fig. 3. DTA curves of $Li_{2.9}Sc_{1.9}Zr_{0.1}(PO_4)_3$ (a) and $Li_{2.9}Sc_{1.8}Y_{0.1}Zr_{0.1}(PO_4)_3$ (b) compounds.

Fig. 3. Dilatometry curves of $Li_{2.9}Sc_{1.9}Zr_{0.1}(PO_4)_3$ (a) and $Li_{2.9}Sc_{1.8}Y_{0.1}Zr_{0.1}(PO_4)_3$ (b) compounds.

Broad peaks in the temperature range 420-510 K for $Li_{2.9}Sc_{1.9}Zr_{0.1}(PO_4)_3$ and 410-520 K for $Li_{2.9}Sc_{1.8}Y_{0.1}Zr_{0.1}(PO_4)_3$ is related to superionic phase transitions in these materials. The peaks at about 1000 K are related to sintering temperature of the ceramics,

also seen from dilatometric curves (Fig. 4). On the other hand no phase transitions of $Li_{2.8}Sc_{1.8}Zr_{0.2}(PO_4)_3$, $Li_{2.8}Sc_{1.7}Y_{0.1}Zr_{0.2}(PO_4)_3$, $Li_3ScB(PO_4)_3$, and $Li_3B_2(PO_4)_3$ materials are observed by DTA or DSC.

SEM images of polished and thermally etched surfaces of $LiCe_{2/3}PO_4$ ceramics sintered for 1 and 3 h are shown in Fig. 4. No significant differences can be seen in the microstructure of the samples sintered at the same temperature varying the sintering duration.

a)   b)
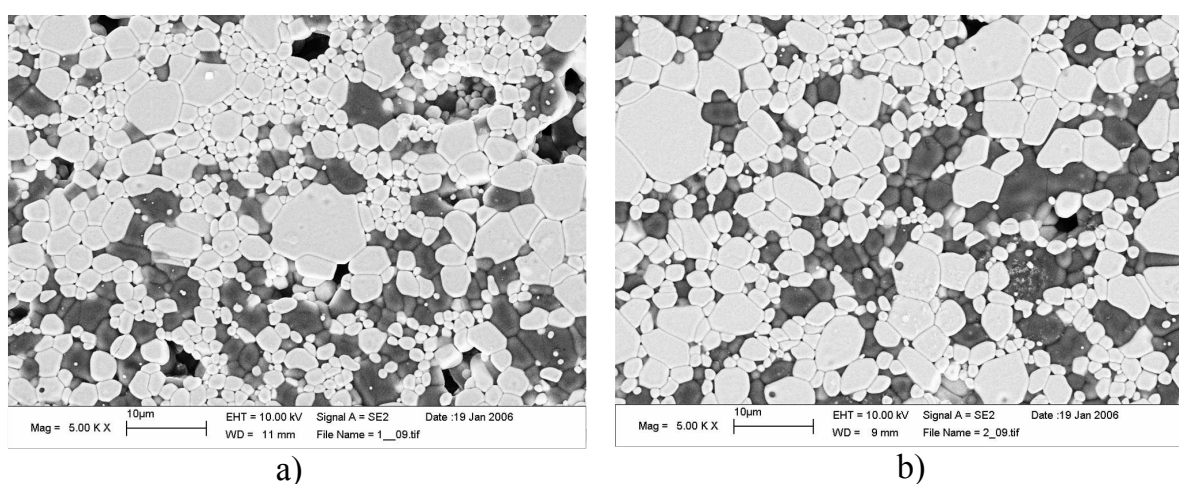
Fig. 4. SEM images of the surfaces of $LiCe_{2/3}PO_4$ ceramics sintered at 1163 K for 1 h (a) and 3 h (b).

SEM images of the surfaces of $Li_{2.8}Sc_{1.8}Zr_{0.2}(PO_4)_3$ ceramics sintered at 1573 K for 1 h and at 1273 K for 6 h are shown in Fig. 5. Much larger crystallites can be seen on the ceramic's surface sintered at higher temperature.
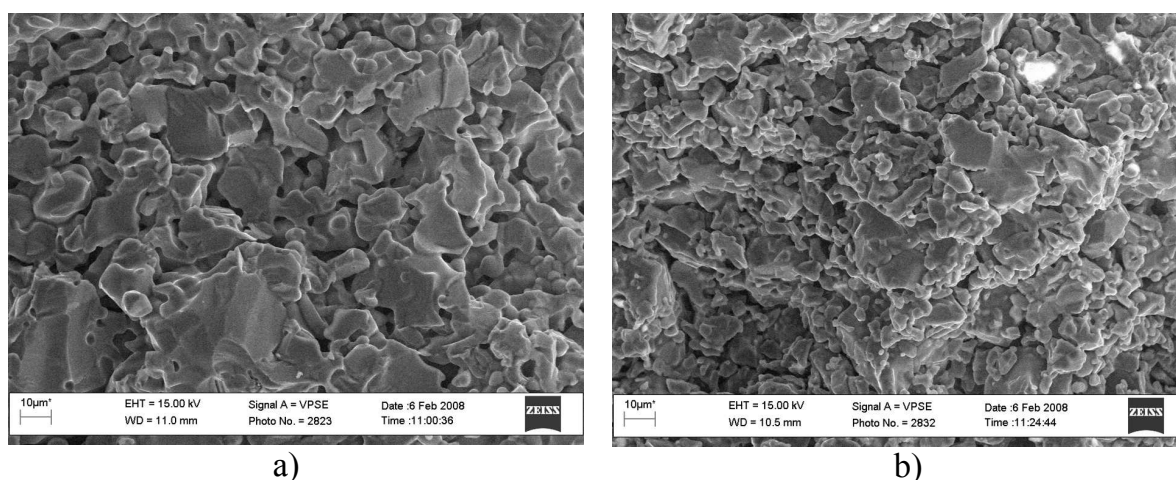

a)   b)

Fig. 5. SEM images of the surfaces of $Li_{2.8}Sc_{1.8}Zr_{0.2}(PO_4)_3$ ceramics sintered at 1573 K for 1 h (a) and at 1273 K for 6 h (b).

Elemental compositions of the ceramics' surfaces were measured by XPS. Spectra of Li 1s photoelectrons of $LiCe_{2/3}PO_4$ ceramic sample before and after influence of E are shown in Fig. 6. The results of elemental composition are summarized in Table 1. The experiment clearly shows that Li^+ ions are mobile in $LiCe_{2/3}PO_4$.
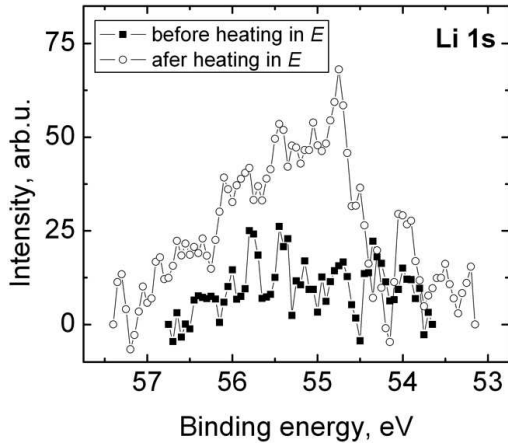

Fig. 6. Li 1s XPS spectra of $LiCe_{2/3}PO_4$ ceramic before and after influence of E.

Table 1. The comparison of element composition of $LiCe_{2/3}PO_4$ compound before and after influence of E.

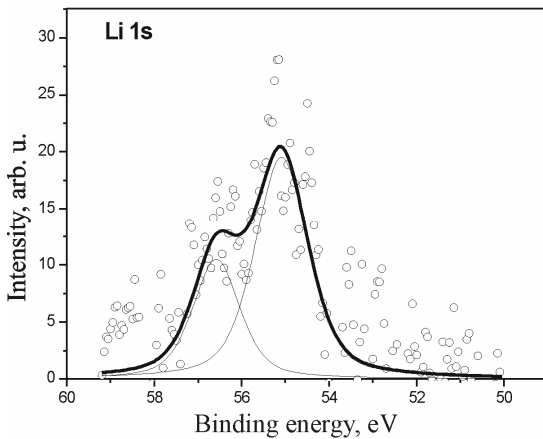|	Atomic %			
	Ce	O	P	Li
Before heating in E	9.5	59.9	16.5	14.1
After heating in E	7.1	50.7	18.4	23.8

Fig. 7. Li 1s XPS spectrum of $Li_{2.9}Sc_{1.9}Zr_{0.1}(PO_4)_3$ ceramic.

Ce 3d photoelectron spectra in $LiCe_{2/3}PO_4$ and $Li_{1/3}Ce_{2/3}PO_4$ ceramics were found the same showing that cerium exists as Ce^{3+} in both compounds. Two sites of lithium are known in the NASICON structure [17]. XPS spectra of Li 1s also show two different sites for lithium in most investigated Li^+-conducting SE. As an example Li 1s XPS spectrum of $Li_{2.9}Sc_{1.9}Zr_{0.1}(PO_4)_3$ compound is shown in Fig. 7.

Frequency dependences of real part of conductivity of $Li_{2.9}Sc_{1.8}Y_{0.1}Zr_{0.1}(PO_4)_3$ ceramic measured by two-electrode method is shown in Fig. 8. Three dispersion regions can be seen from the spectra and the frequency ranges of the dispersions shift towards higher frequencies while temperature is increased. The dispersions have been attributed

to ionic transport in bulk, grain boundaries of the ceramics and to electrode–SE interfaces. Bulk (σ_b) and total

$$\sigma_{tot} = \frac{1}{\rho_b} + \frac{1}{\rho_{gb}} = \frac{\sigma_b \cdot \sigma_{gb}}{\sigma_b + \sigma_{gb}} \qquad (3)$$

ionic conductivities were estimated from impedance plots in complex plane (Fig. 9) or alternatively from $\sigma''(\sigma')$ plots.
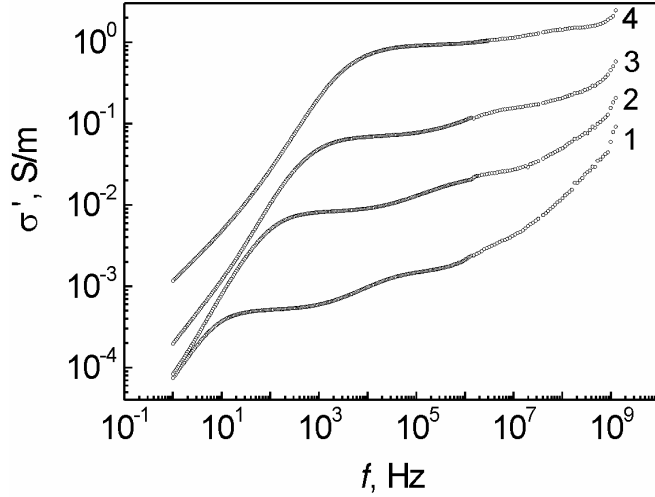

Fig. 8. Frequency dependences of the real part of conductivity of $Li_{2.9}Sc_{1.8}Y_{0.1}Zr_{0.1}(PO_4)_3$ ceramic measured at different temperatures: 1 – 320 K, 2 – 370 K, 3 – 420 K, 4 – 520 K.
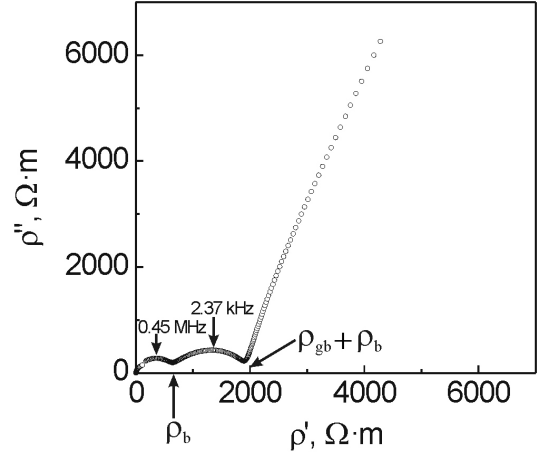
Fig. 9. Complex impedance plot of $Li_{2.9}Sc_{1.8}Y_{0.1}Zr_{0.1}(PO_4)_3$ ceramic measured at 320 K.

Temperature dependences of σ_b and σ_{tot} of the studied SE change according to Arrhenius law

$$\sigma_{b,tot} = \sigma_0 \exp\frac{-\Delta E_{b,tot}}{kT} \qquad (4)$$

where T – temperature, σ_0 – preexponential factor, $\Delta E_{b,tot}$ – activation energies of bulk and total conductivities respectively, k – Boltzmann's constant. Temperature dependences of conductivities of $Li_{1+x}Sc_xZr_{2-x}(PO_4)_3$, $Li_{1+x}Ge_{2-2x}Al_xTi_x(PO_4)_3$, and $Li_{1+x}Zr_{2-2x}Al_xTi_x(PO_4)_3$ (where x = 0.1, 0.2, 0.3) SE are presented in Fig. 10–13. Activation energies of conductivities are summarized in Table 2. In general σ_b and σ_{tot} increases and the activation energies of σ_b (ΔE_b) decreases with increasing stoichiometric factors.
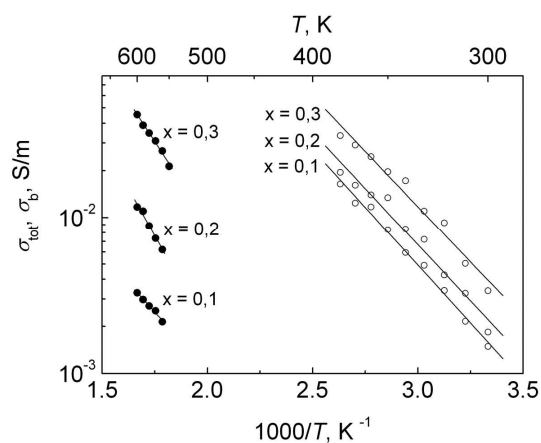
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Fig. 10. Temperature dependences of bulk (○) and total (●) conductivities of $Li_{1+x}Sc_xZr_{2-x}(PO_4)_3$ (where x = 0.1, 0.2, 0.3) ceramics.
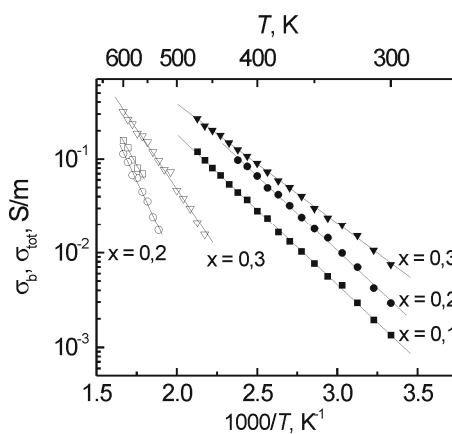

Fig. 11. Temperature dependences of bulk (closed symbols) and total (open symbols) conductivities of $Li_{1+x}Ge_{2-2x}Al_xTi_x(PO_4)_3$ (where x = 0.1, 0.2, 0.3) ceramics.
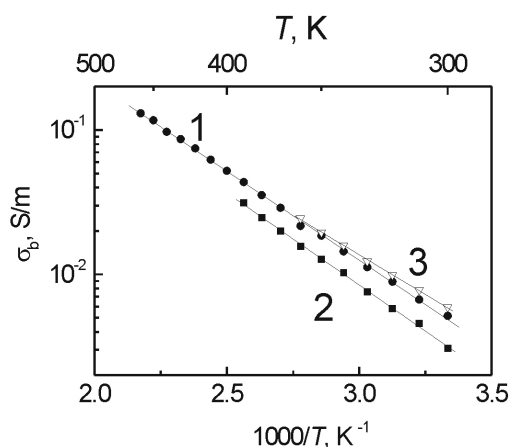

Fig. 12. Temperature dependences of bulk conductivities of $Li_{1.1}Zr_{1.8}Al_{0.1}Ti_{0.1}(PO_4)_3$ (1), $Li_{1.2}Zr_{1.6}Al_{0.2}Ti_{0.2}(PO_4)_3$ (2) and $Li_{1.3}Zr_{1.4}Al_{0.3}Ti_{0.3}(PO_4)_3$ (3) ceramics.
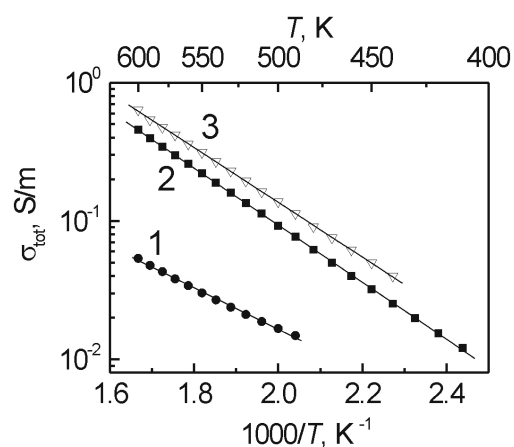
Fig. 13. Temperature dependences of total conductivities of $Li_{1.1}Zr_{1.8}Al_{0.1}Ti_{0.1}(PO_4)_3$ (1), $Li_{1.2}Zr_{1.6}Al_{0.2}Ti_{0.2}(PO_4)_3$ (2) and $Li_{1.3}Zr_{1.4}Al_{0.3}Ti_{0.3}(PO_4)_3$ (3) ceramics.

Temperature dependences of total conductivities of $Li_3Ce_2(PO_4)_3$ and $Li_3Sc_{0.3}Ce_{1.7}(PO_4)_3$ ceramics are shown in Fig. 14. The ionic conductivity of $Li_3Ce_2(PO_4)_3$ was increased by partial substitution of Ce^{3+} by Sc^{3+}. The total conductivity of the ceramics is also increased slightly by increasing sintering duration.

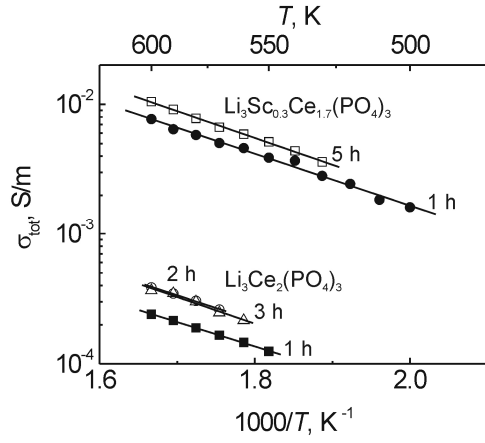Fig. 14. Temperature dependences of total conductivities of $Li_3Ce_2(PO_4)_3$ and $Li_3Sc_{0.3}Ce_{1.7}(PO_4)_3$ ceramics sintered for different duration.

Table 2. Activation energies of bulk conductivities (ΔE_b) and total conductivities (ΔE_{tot}).

Composition	ΔE_b, eV	ΔE_{tot}, eV
$Li_{1.1}Sc_{0.1}Zr_{1.9}(PO_4)_3$	0.30	0.30
$Li_{1.2}Sc_{0.2}Zr_{1.8}(PO_4)_3$	0.29	0.49
$Li_{1.3}Sc_{0.3}Zr_{1.7}(PO_4)_3$	0.28	0.41
$Li_{1.1}Zr_{1.8}Al_{0.1}Ti_{0.1}(PO_4)_3$	0.25	0.30
$Li_{1.2}Zr_{1.6}Al_{0.2}Ti_{0.2}(PO_4)_3$	0.26	0.41
$Li_{1.3}Zr_{1.4}Al_{0.3}Ti_{0.3}(PO_4)_3$	0.22	0.40
$Li_{1.1}Ge_{1.8}Al_{0.1}Ti_{0.1}(PO_4)_3$	0.32	0.62
$Li_{1.2}Ge_{1.6}Al_{0.2}Ti_{0.2}(PO_4)_3$	0.32	0.73
$Li_{1.3}Ge_{1.4}Al_{0.3}Ti_{0.3}(PO_4)_3$	0.25	0.51

The anomalies in σ_b temperature dependences of $Li_3Sc_2(PO_4)_3$ can be associated to $\alpha \leftrightarrow \beta \leftrightarrow \gamma$ phase transitions [3]. Temperature dependences of bulk conductivities of $Li_3Sc_{2-x}B_x(PO_4)_3$ SE are shown in Fig. 15.

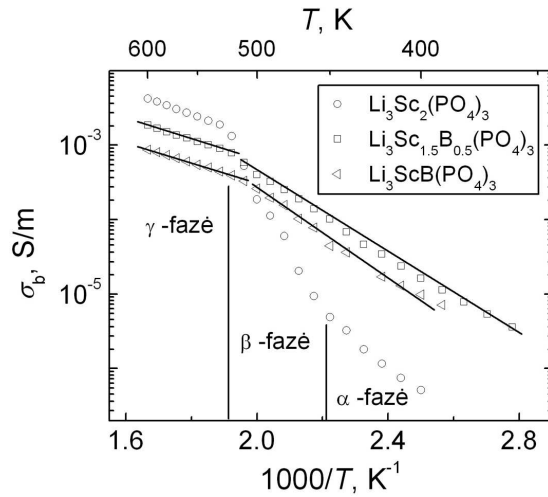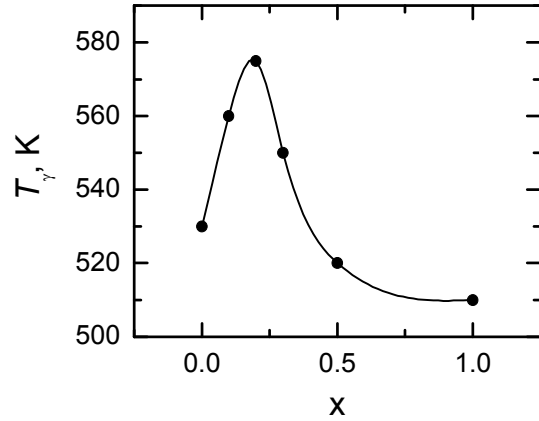Fig. 15. Temperature dependences of bulk conductivities of $Li_3Sc_{2-x}B_x(PO_4)_3$ (where x = 0, 0.5, 1) ceramics.

Fig. 16. Dependence of transition temperature to γ-phase on stoichiometric parameter of $Li_3Sc_{2-x}B_x(PO_4)_3$ compounds.

Only a change of ΔE_b can be observed in $\sigma_b(1/T)$ plot for $Sc^{3+} \rightarrow B^{3+}$ substituted compounds with no rapid increase of conductivity. This fact means that the samples $Li_3Sc_{2-x}B_x(PO_4)_3$ where $x \geq 0.5$ are in superionic phase in the studied temperature range, but transition temperature to γ-phase (T_γ) depends on stoichiometric factor x (Fig. 16).

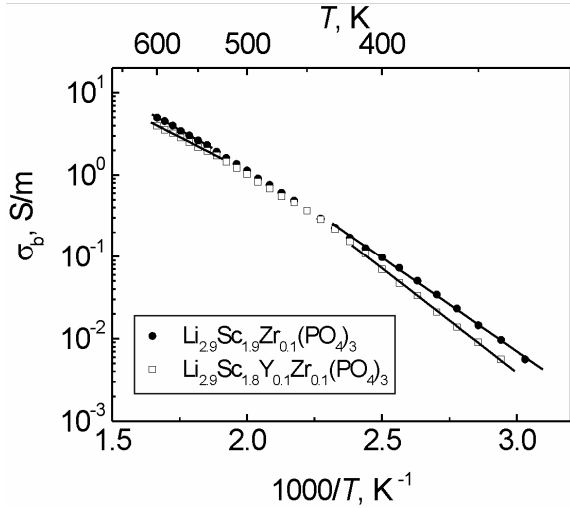Fig. 16. Temperature dependences of bulk conductivities of $Li_{2.9}Sc_{1.9}Zr_{0.1}(PO_4)_3$ and $Li_{2.9}Sc_{1.8}Y_{0.1}Zr_{0.1}(PO_4)_3$ceramics.

Phase transition temperature range of $Li_{2.9}Sc_{1.9}Zr_{0.1}(PO_4)_3$ and $Li_{2.9}Sc_{1.8}Y_{0.1}Zr_{0.1}(PO_4)_3$ observed from temperature dependences of σ_b (Fig. 17) correlate well with DTA results, while no $\sigma_b(1/T)$ anomalies can be seen for $Li_{2.8}Sc_{1.7}Y_{0.1}Zr_{0.2}(PO_4)_3$ and $Li_{2.8}Sc_{1.8}Zr_{0.2}(PO_4)_3$ compounds.

One relaxational dispersion was observed for YSZ films sputtered by magnetron on alloy-600 and Ni-cermet substrates. The dispersion is related to $V_O^{\bullet\bullet}$ conduction. The film sputtered for 1 h on alloy-600 substrate heated at 533 K with 0 offset bias was found to be homogeneous, at 800 K $\sigma = 0.01$ S/m and $\Delta E = 0.6$ eV.

Complex impedance plot of a symmetrical SOFC (Ni-CGO/YSZ/Ni-CGO) measured at 723 K is presented in Fig. 17.

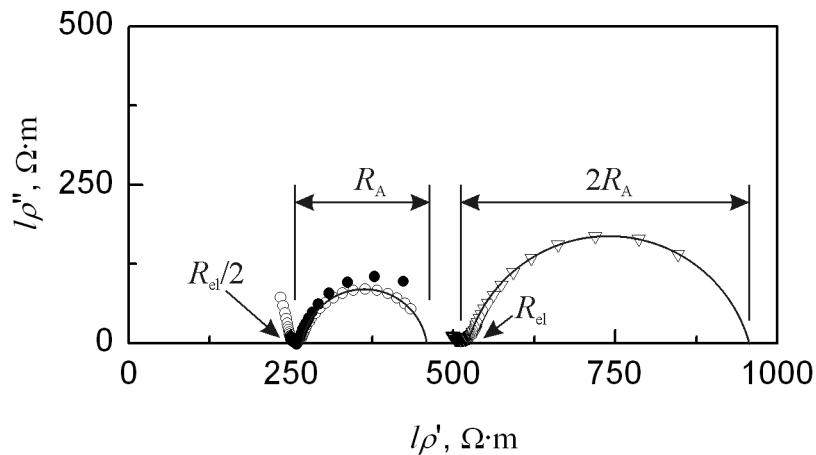Fig. 17. Complex impedance plot of Ni-CGO/YSZ/Ni-CGO cell, measured by two-electrode ($\triangledown$) and three electrode ($\circ$ and $\bullet$) methods at 723 K. R_A − polarization resistance of the anode, R_{el} − resistance of YSZ electrolyte.

Half-cell (three electrode) measurements allows one to determine polarisation resistance of a single electrode while the measurement by two-electrode method corresponds to the sum of resistances of two electrodes. R_A of 60/40 vol.% Ni-CGO anode is lower compared to pure Pt anode (Fig. 18). R_A were also dependent on the crystallization temperature of the sprayed anodes. 10 h annealing at 923 K corresponded to crystallite sizes of 5 nm and at 1273 K − 53 nm. R_A versus annealing temperature (T_{kep}) is shown in Fig. 19.
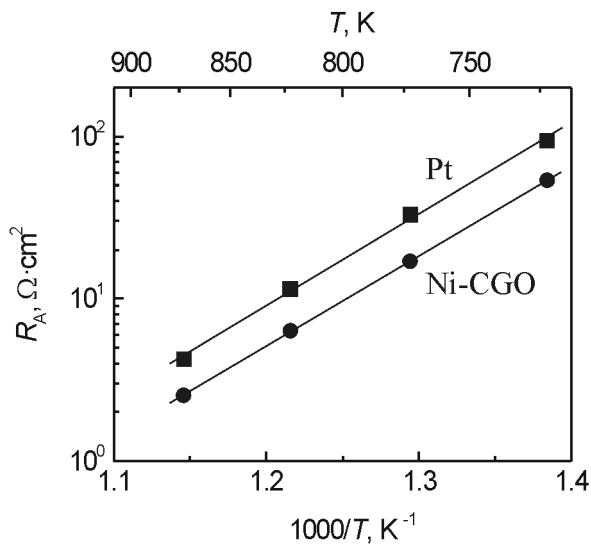
Fig. 18. Temperature dependences of polarization resistances of 60/40 vol.% Ni-CGO and Pt on CGO substrates.
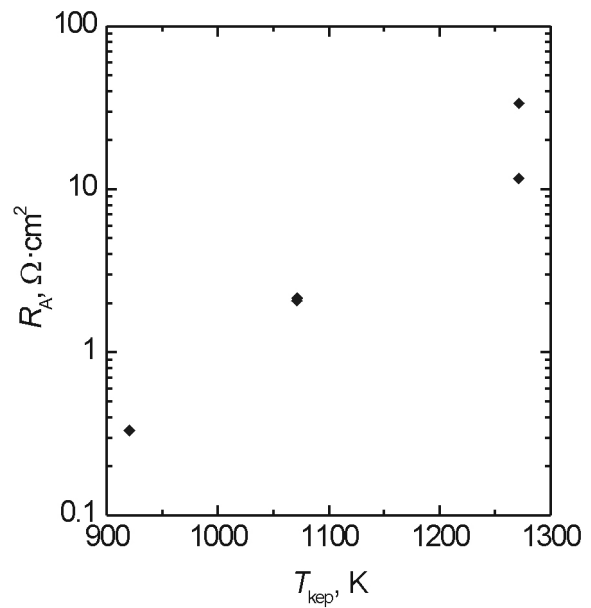
Fig. 19. Polarization resistances of Ni-CGO anodes on CGO substrates versus annealing temperatures of the films (measured at 823 K).

The real part of dielectric permittivity (ε') of the studied SE has been calculated at 1 GHz frequency, which is higher than Maxwell's relaxation frequency. Generally ε' is caused by polarization of ionic migration, vibrations of lattice and electronic polarization. ε' increases with increasing temperature, as is normally observed for most SE.

Conclusions

NASICON and LLTO-type lithium SE have been synthesized by solid state reaction and their ceramics were sintered. ZrO_2-8 mol% Y_2O_3 films have been sputtered by magnetron under different conditions. Amorphous NiO-CGO films have been formed by spray pyrolysis, afterwards followed crystallization of the films and NiO reduction to metallic Ni. Various methods were used for the investigation: XRD, XPS, DTA/TGA SEM, IS. In summary the following conclusions have been made:

1. It has been shown by XPS that $LiCe_{2/3}PO_4$ ceramic is Li^+-ion conductor. Ionic conductivity of $LiCe_{2/3}PO_4$ ceramic measured by IS at 600 K is $2.4 \cdot 10^{-4}$ S/m and ionic conductivity of $Li_3Sc_{0.3}Ce_{1.7}(PO_4)_3$ is $7.7 \cdot 10^{-3}$ S/m.

2. Phase transition temperature to superionic γ-phase in $Li_3Sc_{2-x}B_x(PO_4)_3$ compound when x = 1 is $T_\gamma = 510$ K. No phase transitions were observed in the studied temperature range in the system $Li_{3-x}Sc_{2-x-y}Y_yZr_x(PO_4)_3$ when x = 0.2.

3. Three relaxational dispersions of electrical properties were observed in investigated lithium SE ceramics. The dispersions have been attributed to ionic transport in bulk, grain boundaries of the ceramics and electrode–SE interfaces.

4. The increase of stoichiometric factor x in the systems $Li_{1+x}Sc_xZr_{2-x}(PO_4)_3$, $Li_{1+x}Zr_{2-2x}Al_xTi_x(PO_4)_3$, and $Li_{1+x}Ge_{2-2x}Al_xTi_x(PO_4)_3$ (where x = 0.1, 0.2, 0.3) leads to the increase of bulk conductivity and the decrease of its activation energy. The highest ionic conductivity at 300 K has been found for $Li_{1.3}Ge_{1.4}Al_{0.3}Ti_{0.3}(PO_4)_3$ ceramic (its $\sigma_b = 7,49 \cdot 10^{-3}$ S/m, $\Delta E_b = 0,25$ eV).

5. The dispersion of electrical properties of ZrO_2-8 mol% Y_2O_3 films was found and attributed to $V_O^{\bullet\bullet}$ transport. Technological conditions of fabrication of YSZ thick films by magnetron sputtering influence their ionic conductivity and its activation energy.

6. Ni-CGO films with nanocrystalline grains are promising for SOFC anode preparation due to lower polarization resistance compared to Pt electrodes. The increase of annealing temperature of NiO-CGO films leads to the increase of crystallites' sizes. The lowest polarization resistance was found for Ni-CGO films with average crystallites' sizes of 5 nm.

7. Dielectric permittivity of Li$^+$ SE ceramics and YSZ thick films increases with increasing temperature, the values of dielectric permittivity depend on material's chemical composition and their stoichiometry.

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Santrauka

Disertacijoje yra nagrinėjama, kokią įtaką ličio katijonų ir deguonies vakansijų kietųjų elektrolitų elektrinėms savybėms daro jų struktūra ir elementinė sudėtis. Darbe yra aprašomos technologinės superjoninių junginių (SJ) keramikų ir sluoksnių gamybos sąlygos, lemiančios jų mikrostruktūrą, bei pateikiami SJ paviršių, temperatūrinio stabilumo ir elektrinių savybių tyrimo rezultatai.

Disertaciją sudaro įvadas, 3 skyriai, išvados ir cituojamos literatūros sąrašas. Įvade yra aprašoma tiriamoji problema, darbo aktualumas ir naujumas, iškeltas tikslas, sprendžiami uždaviniai bei pateikiami ginamieji teiginiai ir darbo aprobacija.

Pirmasis skyrius yra literatūros apžvalga. Čia yra apžvelgiamos NASICON tipo $LiM_2^{IV}(PO_4)_3$, $Li_3M_2^{III}(PO_4)_3$ (čia: M^{IV} – keturvalentis, o M^{III} – trivalentis cheminis elementas) ir perovskito tipo $Li_{3x}La_{2/3-x}TiO_3$ superjoninių medžiagų kristalinės struktūros bei elektrinės savybės. Analizuojami NASICON struktūrinio tipo medžiagose vykstančių fazinių virsmų į superjoninę fazę metu vykstantys struktūros pokyčiai, lemiantys didelį medžiagos joninio laidumo atsiradimą ir elemento M kaitos įtaka joniniam SJ laidumui. Apžvelgiamos deguonies vakansijų laidininkų ZrO_2 ir CeO_2, legiruotų įvairiais kitais oksidais, kristalinių struktūrų ypatumai, parodoma priemaišų kiekio įtaka deguonies vakansijų laidumui šių superjonikų keramikose.

SJ gamybos technologinės sąlygos ir jų tyrimo metodai yra aprašomi antrajame skyriuje. Ličio jonų kietieji elektrolitai buvo pagaminti kietųjų fazių reakcijų metodu ir kepintos jų keramikos, parenkant skirtingas keramikų gamybos sąlygas. YSZ sluoksniai buvo pagaminti magnetroninio dulkinimo metodu, o Ni-CGO sluoksniai – purškimo pirolizės metodu bei vėliau kristalizuojami. Superjoninių medžiagų tyrimams buvo naudoti Rentgeno spindulių difrakcijos, temperatūrinės analizės (DTA/TGA), skenuojančios elektroninės mikroskopijos, Rentgeno spinduliais sužadintų fotoelektronų spektroskopijos (XPS) ir kompleksinės varžos spektroskopijos metodai.

Trečiajame skyriuje yra pateikiami tyrimų rezultatai. Tirti Li^+ SJ priklauso monoklininei, ortorombinei arba romboedrinei singonijoms, o jų struktūra yra NASICON tipo. Yra parodoma, kad keramikų mikrostruktūra labiausiai priklauso nuo jų kepinimo temperatūros, o keramikų kepinimo trukmė jų kristalitų dydžiams įtakos praktiškai neturi. $LiCe_{2/3}PO_4$ keramiką paveikus elektriniu lauku, XPS buvo parodyta, kad šioje medžiagoje vyksta Li^+ jonų pernaša. Be to, Li 1s XPS spektrą galima išskaidyti į dvi dedamąsias, kurias galima būtų susieti su žinomomis dvejomis padėtimis NASICON struktūroje.

Kompleksinės varžos spektroskopijos metodu buvo ištirtos Li^+ laidžiųjų keramikų ir deguonies vakansijų sluoksnių elektrinės savybės. Parodyta, kad sistemose $Li_{1+x}Sc_xZr_{2-x}(PO_4)_3$, $Li_{1+x}Zr_{2-2x}Al_xTi_x(PO_4)_3$ ir $Li_{1+x}Ge_{2-2x}Al_xTi_x(PO_4)_3$ (čia x = 0,1, 0,2, 0,3), didinant stechiometrijos faktorių x, didėja kristalitiniai keramikų laidžiai, o jų aktyvacijos energijos mažėja. $LiCe_{2/3}PO_4$ keramikos laidis taip pat padidėja įvykdžius dalinį pakeitimą $Ce^{3+} \rightarrow Sc^{3+}$. $Li_3Sc_{2-x}B_x(PO_4)_3$ junginiuose vykstančio superjoninio fazinio virsmo temperatūra priklauso nuo stechiometrijos faktoriaus x. Mažiausia fazinio virsmo į superjoninę γ fazę temperatūra šioje sistemoje buvo gauta kai x = 1. $Li_{3-x}Sc_{2-x-y}Y_yZr_x(PO_4)_3$ sistemoje kai x = 0,1, y = 0, 0,1 temperatūrinėse kristalitinio laidžio prieklausose yra stebimos anomalijos, susijusios su superjoniniais faziniais virsmais šiose medžiagose, o kai x = 0,2 tirtame temperatūrų intervale faziniai virsmai nevyksta.

ZrO_2-8 mol% Y_2O_3 sluoksniuose buvo aptikta elektrinių parametrų dispersija, susijusi su deguonies vakansijų pernaša. Magnetroninio dulkinimo metodu suformuotų YSZ storųjų sluoksnių SOFC deguonies membranų joninis laidis ir šio laidžio aktyvacijos energija priklauso nuo jų paruošimo technologinių sąlygų.

Didinant NiO-CGO sluoksnių, suformuotų purškimo pirolizės metodu, atkaitinimo temperatūrą didėja kristalitai. Mažiausia poliarizacine varža pasižymėjo Ni-CGO sluoksniai, kurių vidutiniai kristalitų dydžiai buvo 5 nm.

Parodyta, kad Li^+ superjoninių keramikų ir YSZ storųjų sluoksnių dielektrinė skvarba keliant temperatūrą didėja.