

ELECTRIC PROPERTIES OF LITHIUM-CONDUCTING SOLID ELECTROLYTE CERAMICS

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The high temperature solid electrolyte $\text{Li}_{1.3}\square_{1.7}\text{Sc}_{0.3}\text{Ce}_{1.7}(\text{PO}_4)_3$ (where \square is an absence of Li^+) compound was synthesized by a solid state reaction and studied by X-ray diffraction at room temperature. At room temperature the investigated compound belong to monoclinic symmetry (space group $\text{P2}_1/\text{n}$) with four formula units in the lattice. The ceramic samples were sintered at 923 K for 1 h. The surface of the ceramics was investigated by SEM and the chemical composition was tested by EDX. Complex impedance spectroscopy was performed in the frequency range from 10^{-1} to $1.2 \cdot 10^9$ Hz in temperature range from 500 to 700 K. Three relaxation dispersions were found. The dispersions are related to the fast Li^+ ion transport in the grain boundaries and grains of the ceramics and to the processes at the Pt electrode–electrolyte interface.

Keywords: ionic conductivity, permittivity, relaxation dispersion, synthesis, ceramic, sintering

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1. Introduction

Highly ion-conducting solids are promising materials for development of high energy batteries [1] and CO_2 sensors [2]. $\text{LiM}_2(\text{PO}_4)_3$ (where $\text{M} = \text{Ge}, \text{Zr}, \text{Ti}$) compounds with Li^+ ion transport were extensively studied because of their high ionic conductivity and chemical stability [3–5]. Esaka et al. reported that the addition of Li^+ ions in YPO_4 compound caused the appearance of the ionic conductivity of $\text{Li}_{3x}\text{Y}_{1-x}\text{PO}_4$ solid solution [6]. Orlova et al. synthesized $\text{LiCe}_2(\text{PO}_4)_3$ and $\text{Li}_3\text{Ce}_{1.5}(\text{PO}_4)_3$ compounds by the liquid-phase method and studied by X-ray diffraction at room and elevated temperatures [7]. These compounds have typical CePO_4 monazite-type structure and belong to monoclinic symmetry (space group $\text{P2}_1/\text{n}$) with four formula units in the lattice [7]. The authors [8] reported that monazite crystals synthesized by hydrothermal method at temperature of 373 and 473 K belong to hexagonal and monoclinic symmetry respectively. The XPS indicate that the phosphorus exists completely in the form of PO_4^{3-} and cerium exists as Ce(III) with no Ce(IV) in all investigated crystals [8].

It was shown that conductivity of $\text{Li}_3\text{Sc}_2(\text{PO}_4)_3$ was

increased by partial isomorphous substitution of three valence Sc^{3+} by B^{3+} [9]. High Li^+ ion conductivity, their low activation energy stimulate the search and investigation of new Li^+ conducting solid electrolyte materials.

In the present work we have performed the partial substitution of Ce^{3+} by Sc^{3+} in the system $\text{Li}_2\text{O}-\text{Ce}_2\text{O}_3-\text{P}_2\text{O}_5$ (stoichiometric compound is $\text{Li}_3\text{Ce}_2(\text{PO}_4)_3$). We report the conditions for the synthesis of the $\text{Li}_{1.3}\square_{1.7}\text{Sc}_{0.3}\text{Ce}_{1.7}(\text{PO}_4)_3$ powder, sintering of the ceramic samples, and the results of the structure investigation of the compound. The electrical properties of the ceramics have been investigated in the frequency range from 10^{-1} to $1.2 \cdot 10^9$ Hz in the temperature range from 500 to 700 K.

2. Experimental

The powder of $\text{Li}_{1.3}\square_{1.7}\text{Sc}_{0.3}\text{Ce}_{1.7}(\text{PO}_4)_3$ was synthesized from mixture of CeO_2 , Li_2CO_3 (purity 99.999%), Sc_2O_3 (99.99%), and $\text{NH}_4\text{H}_2\text{PO}_4$ (extra pure) by solid state reaction. The mixture was milled as emulsion with ethyl alcohol in a planetary mill with one milling ball of 52 mm in diameter and then heated at

723 K for 3 h. Thereafter the mixture was milled, heated at 1093 K for 1 h (in such a system at the temperatures above 773 K a transition of Ce^{4+} to Ce^{3+} takes place), milled again, and heated at 1093 K for 3 h. Finally, the mixture was milled for 8 h and dried at temperature 393 K for 24 h. The chemical analysis has shown that the synthesized compound has an absence of Li^+ $\square = 1.7$.

The structure parameters were obtained at room temperature from the X-ray powder diffraction patterns recorded with a step of 1°min^{-1} in the region $2\Theta = 6 \dots 80^\circ$ using $\text{Cu K}\alpha_1$ radiation.

The powder was uniaxially cold pressed at 300 MPa. The sintering of the ceramics was conducted in air at temperature $T = 923$ K for 1 h.

The surface of the ceramics was investigated by SEM (Leo 1530). For the SEM investigation the surface of the ceramic sample was polished using suspension with $1 \mu\text{m}$ diamond particles and thermally etched for 1.5 h at 873 K with 10 K/min heating and cooling rates. The average grain size of the ceramic samples was estimated from SEM image using the program LINC which is based on the intercept method [10]. Noran Vantage EDX detector was used to record EDX spectra.

Complex conductivity $\tilde{\sigma} = \sigma' + i\sigma''$, complex impedance $\tilde{Z} = Z' + iZ''$, and complex dielectric permittivity $\tilde{\epsilon} = \epsilon' + i\epsilon''$ were measured while cooling the sample from 700 down to 500 K. In the frequency range from 10^{-1} to 10^5 Hz the impedance measurements were conducted by impedance measurement unit (IM6, Zahner Electric) by two electrode method and the temperature was stabilized by Eurotherm. The measurements in a frequency range from 10^6 to $1.2 \cdot 10^9$ Hz were performed by coaxial impedance spectrometer set-up [11]. Pt paste was used to form electrodes on the ceramic samples. The measurements were carried out in air.

Table 1. X-ray powder diffraction data for $\text{Li}_{1.3}\square_{1.7}\text{Sc}_{0.3}\text{Ce}_{1.7}(\text{PO}_4)_3$ compound at room temperature.

$2\Theta, ^\circ$	$d, \text{\AA}$	hkl	$I/I_0, \%$
17.02	5.21	-1 0 1	14
18.41	4.82	1 1 0	7
18.90	4.69	0 1 1	17
21.22	4.18	-1 1 1	31
21.60	4.111	1 0 1	14
25.08	3.548	1 1 1	16
25.32	3.515	0 2 0	17
26.92	3.309	2 0 0	66
28.75	3.103	1 2 0	100
29.83	2.9928	2 1 0	14
30.16	2.9608	-2 1 1	6
31.12	2.8716	0 1 2; -1 1 2	74
34.42	2.6035	-2 0 2	17
36.78	2.4416	-2 1 2	16
37.30	2.4088	2 2 0	6
41.08	2.1955	0 3 1	17
42.10	2.1446	-3 1 1	29
42.34	2.1330	2 2 1	18
46.00	1.9714	2 1 2	20
46.70	1.9435	3 0 1	6
47.80	1.9013	-2 3 1	11
48.44	1.8777	-1 3 2	23
50.63	1.8015	0 2 3	8
51.72	1.7660	-1 3 2	14
52.40	1.7447	1 3 2	17
52.80	1.7324	-2 2 3	8
53.90	1.6996	-4 0 1; 1 4 0	6
55.55	1.6530	4 0 0	3

3. Results and discussion

The results of the X-ray diffraction study have shown that $\text{Li}_{1.3}\square_{1.7}\text{Sc}_{0.3}\text{Ce}_{1.7}(\text{PO}_4)_3$ powder is mainly single phase material. The corresponding X-ray powder diffraction pattern at room temperature is presented in Fig. 1. The X-ray powder diffraction data are listed in Table 1. The $\text{Li}_{1.3}\square_{1.7}\text{Sc}_{0.3}\text{Ce}_{1.7}(\text{PO}_4)_3$ compound belongs to the monoclinic symmetry (space group $\text{P}2_1/\text{n}$) with four formula units in the lattice. The lattice parameters were found to be $a = 6.8001(13) \text{\AA}$,

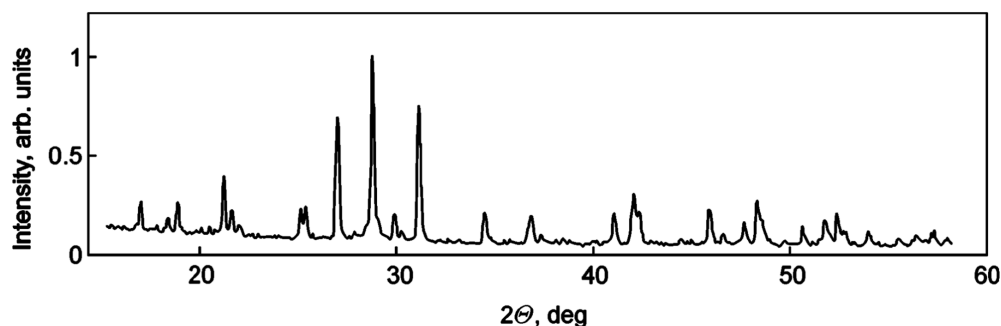


Fig. 1. X-ray diffraction pattern of the $\text{Li}_{1.3}\square_{1.7}\text{Sc}_{0.3}\text{Ce}_{1.7}(\text{PO}_4)_3$ powder.

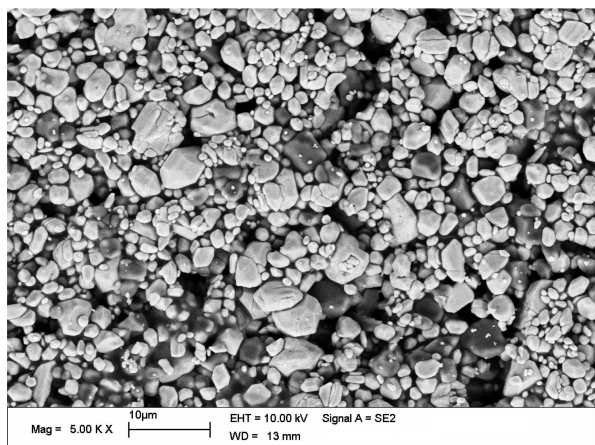


Fig. 2. SEM image of the $\text{Li}_{1.3}\square_{1.7}\text{Sc}_{0.3}\text{Ce}_{1.7}(\text{PO}_4)_3$ ceramic surface.

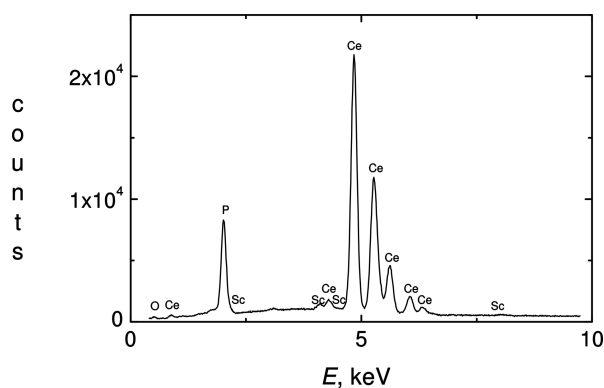


Fig. 3. EDX spectra of the $\text{Li}_{1.3}\square_{1.7}\text{Sc}_{0.3}\text{Ce}_{1.7}(\text{PO}_4)_3$ ceramic grain.

$b = 7.0294(14) \text{ \AA}$, $c = 6.4737(14) \text{ \AA}$, $\beta = 103.468(21)^\circ$, and the unit cell volume is $V = 300.93 \text{ \AA}^3$. The theoretical density of the compound was found to be $d_{X\text{-ray}} = 4.01 \text{ g/cm}^3$. The average grain size of the obtained powder was calculated from X-ray powder diffraction pattern according to Scherer formula:

$$D = \frac{K \lambda}{(\Delta 2\theta) \cos \Theta_0},$$

where D is a particle size, a constant $K = 0.9$, the wavelength of the $\text{Cu K}\alpha_1$ radiation $\lambda = 1.5418 \text{ \AA}$, Θ_0 is an angle of peak intensity, $\Delta 2\theta$ is a width of peak at half of intensity. The average grain size of $\text{Li}_{1.3}\square_{1.7}\text{Sc}_{0.3}\text{Ce}_{1.7}(\text{PO}_4)_3$ was $0.41 \text{ }\mu\text{m}$.

The density of the ceramics was found to be 81% of the theoretical density of the compound. SEM image of the studied ceramic sample is presented in Fig. 2. The average grain size of the ceramics determined was $2.2 \text{ }\mu\text{m}$. A grain intersection to grain size factor of 1.56 was used [10]. EDX spectrum has shown the sample to be free of foreign elements (Fig. 3).

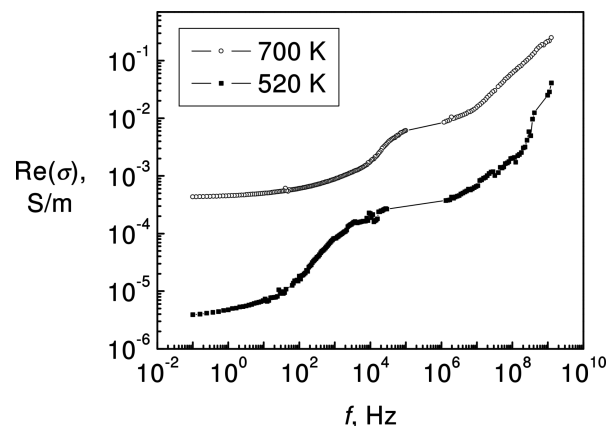


Fig. 4. Frequency dependences of the real part of conductivity of $\text{Li}_{1.3}\square_{1.7}\text{Sc}_{0.3}\text{Ce}_{1.7}(\text{PO}_4)_3$ ceramics at different temperatures.

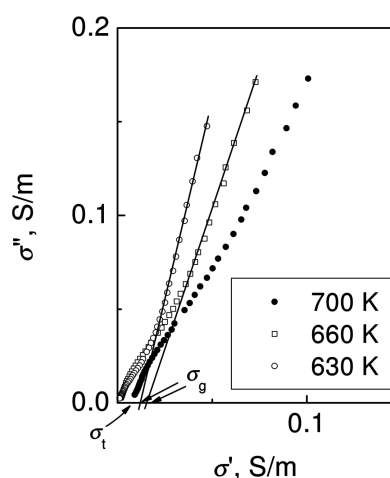


Fig. 5. Complex plane plots of conductivity of $\text{Li}_{1.3}\square_{1.7}\text{Sc}_{0.3}\text{Ce}_{1.7}(\text{PO}_4)_3$ ceramics at different temperatures.

The impedance investigation of the ionic conductivity in the wide frequency and in the broad temperature ranges has an advantage because it allows separating all three charge carrier transport processes in grains, grain boundaries of the ceramics, and in the electrode–solid electrolyte interface [12]. The characteristic frequency dependences of the real part of $\tilde{\sigma}$ of $\text{Li}_{1.3}\square_{1.7}\text{Sc}_{0.3}\text{Ce}_{1.7}(\text{PO}_4)_3$ ceramics at different temperatures are shown in Fig. 4. Three dispersion regions were found in σ' spectra. All dispersion regions shift towards higher frequencies with increase of the temperature. The low frequency dispersion ranges of 10^2 – 10^4 Hz at temperature $T = 520 \text{ K}$ and 10^4 – 10^5 Hz at temperature $T = 700 \text{ K}$ are related to the blocking Pt electrodes. The temperature dependences of total (σ_t) and grain (σ_g) conductivities of $\text{Li}_{1.3}\square_{1.7}\text{Sc}_{0.3}\text{Ce}_{1.7}(\text{PO}_4)_3$ ceramics were derived from complex plots of $\tilde{\sigma}(f)$ at different temperatures. The characteristic complex conductivity plots of the ceramic

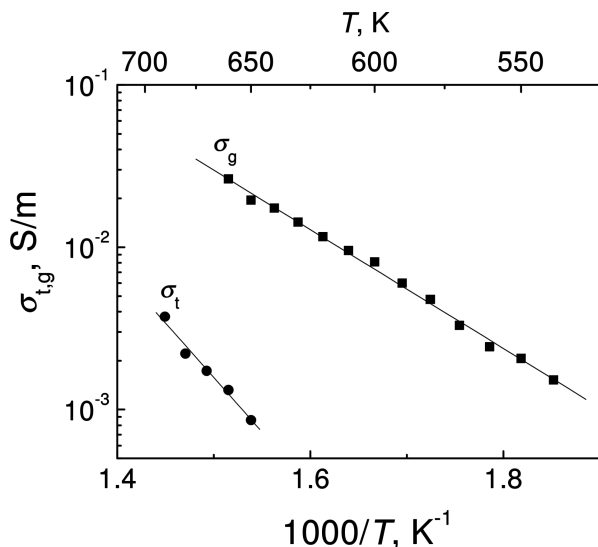


Fig. 6. Temperature dependences of total and grain conductivities of $\text{Li}_{1.3}\square_{1.7}\text{Sc}_{0.3}\text{Ce}_{1.7}(\text{PO}_4)_3$ ceramics.

sample are shown in Fig. 5. Higher frequency part of the obtained spectra may be attributed to the relaxation in grains, while lower frequency part corresponds to grain boundary processes as in a wide range of other solid electrolyte ceramics [13–16]. σ_t and σ_g are indicated with arrows in this graph. At 650 K the values of total and grain conductivities of the investigated ceramics were found to be $\sigma_t = 8.59 \cdot 10^{-4}$ S/m and $\sigma_g = 1.95 \cdot 10^{-3}$ S/m respectively. The temperature dependences of σ_t and σ_g of the ceramic sample are shown in Fig. 6. The activation energies of σ_t and σ_g were found from the slopes of the Arrhenius plots. The activation energy of total conductivity is $\Delta E_t =$

1.34 eV and the activation energy of grain conductivity is $\Delta E_g = 0.73$ eV.

The temperature dependences of the real part of dielectric permittivity ϵ' and dielectric losses $\tan \delta$ were investigated at a frequency of 1 GHz. This frequency is higher than Maxwell relaxation frequency $f_M = \sigma_g / (\epsilon' \epsilon_0)$ (where $\epsilon_0 = 8.85 \cdot 10^{-12}$ F/m is dielectric constant of the vacuum). At 550 K temperature the ω_M of the ceramics was found to be 38.7 MHz. The temperature dependences of ϵ' and $\tan \delta$ of $\text{Li}_{1.3}\square_{1.7}\text{Sc}_{0.3}\text{Ce}_{1.7}(\text{PO}_4)_3$ ceramics are shown in Fig. 7. At 550 K $\epsilon' = 6.03$ and $\tan \delta = 0.095$. The increase of the values of ϵ' with temperature of the investigated compound can be caused by contribution of the migration polarization of lithium ions, vibration of lattice, and electronic polarization. The increase of $\tan \delta$ with temperature is related to the contribution of conductivity in the investigated temperature region.

4. Conclusions

The solid electrolyte $\text{Li}_{1.3}\square_{1.7}\text{Sc}_{0.3}\text{Ce}_{1.7}(\text{PO}_4)_3$ compound has been synthesized by solid phase reactions and studied by the X-ray powder diffraction. The investigated compound belongs to monoclinic symmetry (space group $P2_1/n$) with 4 formula units in the lattice. The ceramics of $\text{Li}_{1.3}\square_{1.7}\text{Sc}_{0.3}\text{Ce}_{1.7}(\text{PO}_4)_3$ were sintered at a temperature of 923 K. The ceramic sample was investigated by complex impedance spectroscopy in the frequency range from 10^{-1} to $1.2 \cdot 10^9$ Hz in the temperature range from 500 to 700 K. Three regions of the relaxation dispersion are related to the

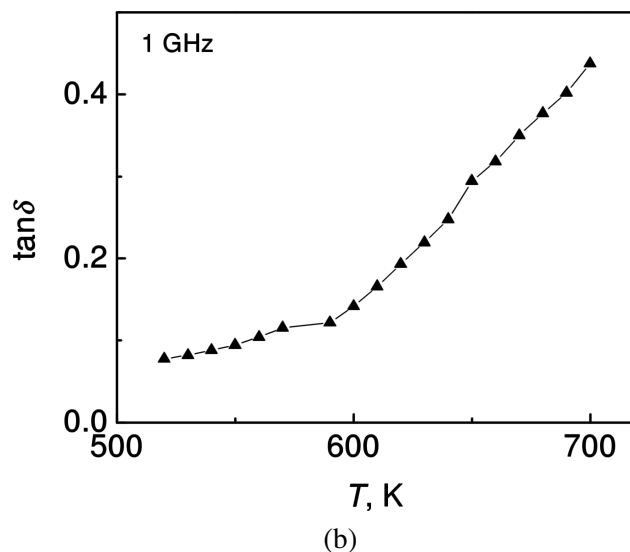
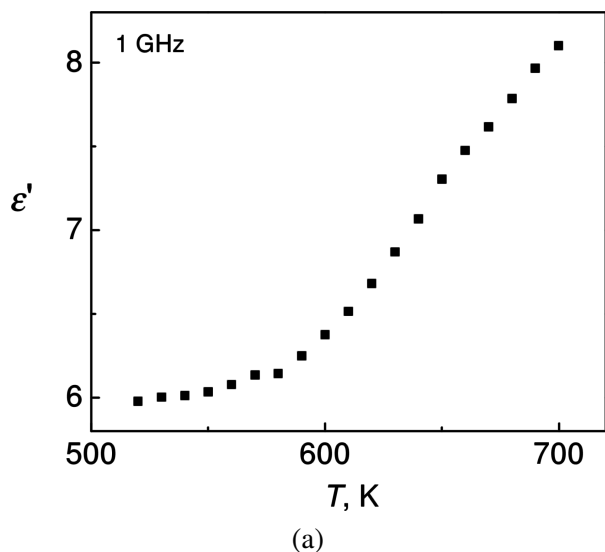


Fig. 7. Temperature dependences of (a) dielectric permittivity and (b) dielectric losses of $\text{Li}_{1.3}\square_{1.7}\text{Sc}_{0.3}\text{Ce}_{1.7}(\text{PO}_4)_3$ ceramics at the 1 GHz frequency.

blocking electrodes (low frequency range) and ion transport in the grain boundaries and grains of the ceramic samples. At 650 K, $\sigma_t = 8.59 \cdot 10^{-4}$ S/m and $\sigma_g = 1.95 \cdot 10^{-3}$ S/m. The values of ε' at room temperature at 1 GHz frequency are related to the polarization process due to migration of Li^+ ions, lattice vibrations, and electronic polarization.

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ELEKTRINĖS LIČIO LAIDŽIŲJŲ KIETŲJŲ ELEKTROLITŲ SAVYBĖS

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Santrauka

Kietasis $\text{Li}_{1.3}\square_{1.7}\text{Sc}_{0.3}\text{Ce}_{1.7}(\text{PO}_4)_3$ (čia \square yra Li^+ trūkumas) elektrolitas buvo susintetintas kietųjų fazių reakcijų metodu. Jo kristalinė struktūra buvo tirta kambario temperatūroje Rentgeno spindulių difrakcijos nuo miltelių metodu. Nustatyta, kad tirtasis junginys priklauso monoklininei singonijai (erdvinė simetrijos grupė $\text{P2}_1/\text{n}$), o jo elementariojoje kristalinėje gardelėje yra 4 formuliniai vienetai. Buvo pagamintos šių kietųjų elektrolitų keramikos. Keramikų elektrinės savybės buvo tirtos impedanso spektroskopijos metodu, matuojant jų pilnutinę varžą, kompleksinį laidį ir

kompleksinę dielektrinę skvarbą 10^{-1} – $1,2 \cdot 10^9$ Hz dažnio elektriniame lauke 500–700 K temperatūros intervale. Tirtose keramikose yra stebimos trys relaksacinio tipo elektrinių parametrų dispersijos, susijusios su blokuojančiais Pt elektrodais, Li^+ jonų pernaša kristalituose ir tarpkristalitinėse terpėse. Esant 650 K temperatūrai, bendrasis keramikos laidis $\sigma_t = 8,59 \cdot 10^{-4}$ S/m ir kristalitinis laidis $\sigma_g = 1,95 \cdot 10^{-3}$ S/m. Didėjant temperatūrai, keramikų ϵ' ir $\tan \delta$ didėja. Keramikų ϵ' dydį lemia ličio jonų migracinė, joninė tamprioji bei elektroninė poliarizacijos. Matuotų kietųjų elektrolitų dielektrinius nuostolius lemia jų joninio laidumo kaita.