Formation of ceramic targets for solid electrolytes sputtering

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Abstract. The results of ceramic targets formation from powders of Li1.3Al0.3Ti1.7(PO4)3 and Li6.4Al0.2La3Zr2O12 solid electrolytes by cold pressing with subsequent high-temperature sintering are presented. Solid electrolyte powders of Li1.3Al0.3Ti1.7(PO4)3 (LATP) with the NASICON structure and Li6.4Al0.2La3Zr2O12 (LLZ) with the garnet structure with high Li-ion conductivity were synthesized by methods protected by patents in the RF, suitable for mass production. The conditions for the formation of dense single-phase targets (14 mm in diameter and 8-10 mm thick) from LATP and LLZ (cubic modification) solid electrolytes were established by X-ray diffraction analysis. The ionic conductivity, Li+ ion transfer number and electronic conductivity of LATP and LLZ ceramic targets were determined by electrochemical impedance spectroscopy and potentiostatic chronoamperometry methods.

1. Introduction

Industrial rechargeable lithium batteries are prone to spontaneous combustion and even explosion due to the flammable liquid organic electrolytes in them. The safety problems of lithium batteries can be solved by using non-flammable solid electrolytes. Despite many years of efforts, only a few groups of ionic conductors were found among thousands of lithium-containing inorganic materials: the family of Li10GeP2S12, garnets Li7La3Zr2O12, Li1+xAlxTi(Ge)2-x(PO4)3 and perovskites Li3+La0.67-xTiO3 [1].

According to President of the Russian Chemists Union V.P. Ivanov at the XXI Mendeleev Congress on General and Applied Chemistry, import of low-tonnage chemistry products to Russia accounts for 90% of market needs. In this connection there is an urgent need to create in Russia own production of such level with the emphasis on import substitution policy.

At present, new effective methods for the synthesis of inorganic solid electrolytes with high lithium-ion conductivity have been developed at the ICTREM RM of the Kola Science Center of the Russian Academy of Sciences. These materials with the NASICON structure of Li1+xAlxTi2-x(PO4)3 (LATP) and Li1+xAlxGe2-x(PO4)3 (LAGP), with the perovskite structure Li3+La0.67-xTiO3 (LLT) and with the garnet structure Li7-3xAlxLa3Zr2O12 (LLZ), which can be used in mass production [2-4]. Since the application as a separator for lithium-air cells with lithium anode and aqueous electrolytes requires stable ceramics in the form of high-density plates, the conditions for making dense thin (600-700 microns) pellets from submicron LATP, LAGP and LLT powders by cold pressing followed by high-temperature sintering were established. However, to reduce the resistance of the solid electrolyte separator layer in new-generation all solid-state batteries ultra-thin films are required, which can be obtained by modern methods: substrate immersion (dip-coating), tape casting, aerosol deposition, radio frequency magnetron
sputtering.

The principal possibility of obtaining LATP films by immersion of sapphire substrate in a water-peroxide solution of a solid electrolyte precursor with glycerol as a film-forming agent was demonstrated [5]. The LATP film formation was carried out as follows. The substrate was dipped into the precursor solution, then pulled at a rate of 0.6 cm/min, air-dried, annealed at 450°C for 15 min and cooled to room temperature. Then the process of applying the solution on the substrate was repeated and the sample was annealed at 800°C for 30 min. X-ray diffraction analysis showed that four reflexes with hkl (012), (104), (113) and (024) crystallographic indices characteristic for LATP were observed in the diffractogram of the sapphire substrate with the applied film.

For the preparation of LATP films (83-85% density), commercially available LATP powders consisting of particles larger than 4-5 µm and containing AlPO₄ as an impurity phase were used in a new ceramic deposition technique by aerosol deposition [6]. Commercially available LATP powders were preground in a ball mill for 30-60 min at 200-250 rpm to reduce the crystallite size to 1 µm, making them suitable for the aerosol deposition techniques.

Lower total conductivity of LAGP film obtained by aerosol deposition is mainly attributed to large grain-boundary resistance between the LAGP nanoparticles in the film. Improvement of film density and the connectivity among the LAGP nanoparticles in the film should be needed to enhance the total conductivity [7]. In order to achieve higher Li⁺ ion conductivity in LLZ solid electrolyte film formed by aerosol deposition, further study is necessary to suppress the formation of the impurity phases (Li₂CO₃, La₂O₃, La₂Zr₂O₇) in LLZ garnet film, particularly by the powder treatment such as the composition, synthesis route, and controlling of the particle size [8].

The authors [9-11] believe that radiofrequency magnetron sputtering of solid electrolytes method has advantages: relatively simple apparatus, low cost, high quality of films, good thickness control and uniform film deposition over relatively large areas. In a recent study [12] thin films of LAGP ~1 µm in thickness were grown by radiofrequency sputtering from powder targets under different conditions with ionic conductivities similar to those reported for bulk ceramic samples. The sample powder was simply prepared from commercial LAGP powder from MTI with nominal composition Li₁₅Al₀₅Ge₁₅(PO₄)₃. LAGP and LLZ solid electrolyte sputtering targets are offered by Toshima Manufacturing (Japan), MTI Co., LTD (China), NEI Corporation, MSE Supplies (USA). These are ceramic plates with a diameter of 5.08 cm and thickness of 0.31 cm at a price of $1300-1600/piece [13].

This paper presents the results of forming proprietary LATP and LLZ ceramic targets of stoichiometric composition by cold-pressing from solid electrolyte powders synthesized by methods [2, 4], which will significantly reduce the cost of the films. Solid electrolytes of nominal composition Li₁₃Al₀₃Ti₁₇(PO₄)₃ (LATP) was synthesized from a liquid-phase peroxide precursor [2]. Al-substituted LLZ samples in the form of a powdered material of the composition of Li₆₄Al₀₂La₃ZrO₁₂ were synthesized by melting the charge with subsequent solid-phase sintering. Due to the use of low-melting crystal hydrates ZrO(NO₃)₂·2H₂O and La(NO₃)₃·6H₂O as starting materials, an increase in the manufacturability of the synthesis method was achieved [4].

2. Experimental methods

The synthesized powders and solid electrolyte targets were characterized by X-ray diffraction analysis, measurement of ionic and electronic conductivity. The phase composition was determined using an XRD-6000 diffractometer (Shimadzu, Japan). The diffractograms were interpreted on the basis of the ICDD PDF-4 database. The specific surface of powders was determined by thermal desorption of nitrogen on an electronic meter of specific surface FlowSorb II 2300 (Micromeritics). The content of elements (lithium, zirconium, lanthanum, aluminum, titanium, and phosphorus) was determined by atomic emission spectrometry with inductively coupled plasma on the device ICPE 9000 (Shimadzu, Japan).

To study the ionic conductivity of the pellets and the targets the dispersion of the complex impedance with the amplitude of the AC signal up to 0.1 V in the frequency range 10⁻²·10⁶ Hz was studied with a Z-2000 impedance meter (Elins). The ionic conductivity (σ) of the pellets and targets was measured
with electrochemical impedance spectroscopy (EIS) in a C/LATP/C or C/LLZ/C symmetric shielded cells at room temperature. The EIS method implies the study of a response of an electrochemical system to a disturbance of a small amplitude in a wide frequency range and is related to the relaxation methods. The blocking graphite electrodes were applied in the form of a thin layer on the ends of LATP (LLZ) pellet (or target). The specific ionic conductivity of LATP (LLZ) was found by extrapolating the impedance hodograph \( Z'' = f(Z) \) to the axis of the active resistances and calculated taking into account the geometric dimensions of LATP (LLZ) pellet (or target) according to the equation:

\[
\sigma = \frac{h}{RS}
\]

where \( h \) is the thickness of the pellet (or target), \( S \) is its area, and \( R \) - its resistance.

The \( Li^+ \) ion transfer number and the value of electronic conductivity were determined by potentiostatic chronoamperometry with a P-8 potentiostat (Elins).

3. Results and discussion

Sintering of solid electrolyte powders compressed from solid electrolytes massive spray targets (14 mm in diameter and 6-8 mm thick) was carried out similarly to sintering of pellets (≥ 10 mm in diameter and 1-2 mm thick). The following sintering mode was set to obtain dense samples. For LATP targets: heating in a muffle furnace MIMP-3P at a rate of 10 deg/min to a temperature of 1000°C and isothermal soaking for 2 h (figure 1a). For LLZ targets: heating (in corundum crucibles under matte powder) in a muffle furnace at a rate of 10 deg/min to a temperature of 1000°C and then heating at a rate of 2 deg/min to 1150°C with isothermal soaking for 8 h (figure 1b).

![Figure 1. Appearance of powder, pellets and targets of LATP (a) and LLZ targets (b).](image)

The correspondence of the LATP target to the chemical composition \( Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3 \) was confirmed by inductively coupled plasma atomic emission spectrometry (\( Li_2O \) content 5.04 wt%, \( Al_2O_3 \) content 3.99 wt%, \( TiO_2 \) content 35.15 wt%, \( P_2O_5 \) content 55.32 wt%).
According to XRD data, LATP targets are monophasic (ICDD PDF-4 00-066-0868). All X-ray reflections of the sample were clearly resolved, and the narrow peaks indicate high crystallinity (figure 2).

Based on the analysis of electrochemical impedance spectra, it was found that the value of specific conductivity of targets corresponds to the values obtained for pellets and it is \( \sim 1 \times 10^{-4} \text{ S/cm} \) (figure 3). Thus, the conditions of target formation for sputtering of LATP solid electrolyte with a density of 80-85\% were determined.

**Figure 2.** LATP solid electrolyte target diffractogram.

**Figure 3.** Impedance hodographs of pellet (a) and target (b) of LATP solid electrolyte at 20°C.
Figure 4. Diffractogram of pellet (a) and target (b) of LLZ solid electrolyte after sintering under the same conditions.

Further it was found that sintering pellets and targets of solid electrolyte LLZ in the same conditions with isothermal aging at 1150°C for 8 h in the first case pellets of cubic modification are formed (figure 4a), and in the case of massive targets weighing 4-5 g samples LLZ represent a mixture of two modifications: tetragonal and cubic (figure 4b).

The tetragonal phase of LLZ can be identified on the X-rays by splitting of the peaks with Miller index 211 at 2θ = 16.5 deg and the peak with Miller index 420 at 2θ = 30.5 deg (most pronounced). The split peak at 2θ = 30.5 deg merges into one well-resolved peak for the cubic LLZ modification (figure 4a). Data from electrochemical impedance spectroscopy can also supplement the XRD results and confirm the presence of tetragonal modification in the LLZ samples.

During the synthesis of LLZ in corundum crucibles, an additional uncontrolled doping of LLZ by Al³⁺-ions occurs as a result of the interaction of the reaction mixture with the crucible walls. At the same sintering mode of pellets and targets pressed from charges of the same batch, LLZ samples were obtained with the same density (within the measurement error). When producing thin pellets, all LLZ samples were of the cubic modification with high ionic conductivity (figure 5). However, the target resistivity was extremely high, which may indirectly indicate the formation of a mixture of the cubic and tetragonal modifications of LLZ. Apparently, the previously established level of Al substitution (x = 0.2) and the duration of sintering at 1150°C were not sufficient to completely stabilize the cubic modification when sintering the massive targets whose weight was almost 10 times higher than the average pellet weight.
Figure 5. Typical impedance hodograph of an LLZ pellet (11 mm in diameter and 1.4 mm thick) (a) and an LLZ target (b) (14 mm in diameter and 7.6 mm thick) at 20°C.

In accordance with the results of X-ray phase analysis in the study of the ion transport of LLZ by electrochemical impedance spectroscopy, significant differences in the values of ionic conductivity for pellets and targets were obtained (figure 5). Additional sintering of targets at 1150°C contributed to a significant decrease in resistivity (3-10 times), which may indicate the transformation of the cubic LLZ modification into tetragonal and provides materials with ionic conductivity ~1-10^{-4} S/cm at room temperature.

Thus, the methods of X-ray phase analysis and spectroscopy of electrochemical impedance established the conditions for the formation of dense single-phase targets for sputtering of solid electrolytes LATP and LLZ with high Li^+-ion conductivity. The Li^+ ion transfer number determined by potentiostatic chronoamperometry in the solid electrolytes LATP and LLZ is in the range of 0.97-0.99, indicating that the materials are purely ionic conductors.

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References
[1] Cao C, Li Z-B, Wang X-L, Zhao X-B and Han W-Q 2014 Frontiers in energy research 2 A.25
[2] Kunshina G B, Gromov O G, Lokshin E P and Kalinnikov V T 2013 Patent RU 2493638 Appl 03.08.2012 Publ 20.09.2013 (In Russ)
[3] Kunshina G B, Bocharova I V and Lokshin E P 2016 Patent RU 2583762 Appl 20.04.2015 Publ 10.05.2016 (In Russ)
[4] Kunshina G B, Bocharova I V and Ivanenko V I 2019 Patent RU 2682325 Appl 02.07.2018 Publ 19.03.2019 (In Russ)
[5] Kunshina G B, Gromov O G, Lokshin E P and Kalinnikov V T 2013 Inorganic Materials 49 95
[6] Popovici D, Nagai H, Fujishima S and Akedo J 2011 J. Amer. Ceram. Soc. 94 № 11 3847
[7] Inada R, Ishida K, Tojo M, Okada T, Tojo T and Sakurai Y 2015 Ceramics International 41 11136
[8] Inada R, Okada T, Bando A, Tojo T and Sakurai Y 2017 Progress in Natural Science: Materials International 27 350
[9] Sun Z, Liu L, Yang B, Li Q, Wu B, Zhao J, Ma L, Liu Y and An H 2020 Solid State Ionics 346 115224
[10] Ling Q, Yu Z, Xu H, Zhu G, Zhang X, Zhao Y and Yu A 2016 Materials Letters 169 42
[11] Tan G, Wu F, Li L, Liu Y and Chen R 2012 J. Phys. Chem. C 116 3817
[12] Mousavi T, Chen X, Doerrer C, Jagger B, Speller SC and Grovenor CRM 2020 Solid State Ionics 354 115397
[13] https://www.msesupplies.com