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Lithium stoichiometry of solid electrolytes based on tetragonal $Li_7La_3Zr_2O_{12}$

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ABSTRACT

Samples of $Li_xLa_3Zr_2O_{8.5+0.5x}$ (x = 6, 7, 8, 9, 10) were synthesized with the citrate–nitrate method. Neutron diffraction studies have shown the presence of lithium carbonate impurities in the synthesized compounds. We propose a simple and effective method to determine the carbonate impurity content in the solid electrolytes. The technique is based on the measurement of the carbon dioxide volume produced from the interaction of the investigated material with acid. Determined in this way, the content of Li_2CO_3 in the synthesized electrolytes $Li_7La_3Zr_2O_{12}$, $Li_8La_3Zr_2O_{12.5}$ and $Li_9La_3Zr_2O_{13}$ are 1.32 ± 0.04, 1.95 ± 0.06 and 3.49 ± 0.10 wt.%, respectively. From the obtained data, the actual lithium content per formula unit of complex oxide was calculated for the synthesized compounds. The composition with $x = 9$ had the highest total conductivity, $\sigma = 7.5 \times 10^{-6}$ S cm^{-1}, at room temperature. All the investigated electrolytes have an activation energy of approximately 50 kJ mol^{-1}.

1. Introduction

Ceramic lithium electrolytes are being considered as one of the alternatives to replace the liquid electrolyte in lithium power sources; this replacement will create safer all-solid-state lithium-ion batteries. The synthesis and study of new lithium ceramics of various compositions with different crystalline structures and high conductivity are of great interest [1,2]. Thangadurai and Weppner were the first to explore novel garnets with the nominal chemical composition $Li_5La_3M_2O_{12}$ (M = Nb, Ta) for fast lithium ion conduction [3]. In later years, work was performed to expand this family of compounds and improve the properties of these compounds. Analyzing a huge number of data, Ramzy and Thangadurai [4] noted that the ionic conductivity of the cubic garnets $Li_xA_3M_2O_{12}$ linearly increases as the amount of lithium per formula unit increases.

For use as a solid electrolyte, the most interesting representative of this family of garnets is the complex oxide $Li_7La_3Zr_2O_{12}$ (LLZ). This compound has two structural forms: cubic and tetragonal. The cubic phase of LLZ has higher conductivity at room temperature than the tetragonal form [5]. However, the synthesis of the cubic LLZ is performed at high temperatures for a long time [6].

In superionic compounds with structural disorder, the charge carriers are the ions themselves rather than vacancies [7]. Because LLZ is a superionic conductor, the electrical conductivity of LLZ will increase as the concentration of lithium ions increase. It is known that the stoichiometry of alkali cations in garnet-type compounds can vary without changing the structure [8]. Most likely, the conductivity of tetragonal LLZ can be increased through the introduction of additional carriers to the structure. However, it is unknown to what extent it is possible to vary the lithium content in the structure of LLZ and how this change in lithium content will affect the properties of the system. The objective of the present work was to synthesize solid electrolytes based on LLZ with different stoichiometric amounts of lithium and to study the structure and transport properties of these electrolytes.

2. Experiment

Samples of $Li_xLa_3Zr_2O_{8.5+0.5x}$ with x = 6, 7, 8, 9, and 10 were synthesized. Li_2CO_3, La_2O_3 and an aqueous solution of $ZrO(NO_3)_2$ were used as the precursors for the citrate–nitrate synthesis. The starting materials were taken in a stoichiometric ratio. These components were dissolved in a mixture of dilute nitric and citric acids. The resulting solution was evaporated at 80 °C to form a transparent gel. The gel was then dried and was pyrolyzed at ~200 °C; this pyrolysis resulted in the formation of black powder.

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The synthesis was performed by increasing the temperature stepwise from 700 °C to 900 °C for 5 h and with calcination at the final temperature for 1 h. After each stage of the synthesis, the mixture of reagents was thoroughly ground in an agate mortar.

X-ray diffraction analysis (XRD) was performed with a Rigaku D-MAX-2200V diffractometer with a vertical goniometer, Cu K_α-radiation and $2\theta = 10–70°$. The XRD patterns of the compounds were compared with those in the PDF-2 database.

Neutron diffraction measurements of $Li_xLa_3Zr_2O_{8.5+0.5x}$ ($x = 7, 8, 9$) at room temperature were performed on the high-resolution powder diffractometer D7a at the research reactor IVV-2M of the Institute of Metal Physics, Ural Branch of the Russian Academy of Sciences. The powdered samples were sealed in cylindrical vanadium containers with diameters of 8 mm. The D7a diffractometer used a double graphite (0 0 2)–Ge (5 1 1) monochromator; the neutron wavelength was 1.5321 Å. The neutron diffraction patterns were recorded over a scattering angle range of 10–125° with a step of 0.05°. The profiles of the diffraction patterns were refined by Rietveld analysis with the FULLPROF program.

The investigated material was treated with aqueous solutions of hydrochloric (HCl) or acetic (CH_3COOH) acids to determine the carbonate impurity content in the solid electrolytes. The volume of carbon dioxide liberated is directly proportional to the amount of carbonate in the sample. This volume of gas was determined with a liquid volumeter (Fig. 1). A saturated aqueous solution of potassium chloride (KCl) was used as the volumetric liquid to prevent the dissolution of CO_2 in the water.

To determine the amount of gas based on Avogadro's law it is necessary to relate the volume of gas liberated during the experiment to the volume at normal conditions:

$$V_0 = \frac{V_T T_0 (P - \Delta - P_V)}{P_0 T}, \qquad (1)$$

where V_0 is the volume of the gas at normal conditions ($T_0 = 273$ K, $P_0 = 760$ Torr), V_T is the volume of the gas liberated during the experiment, T is the temperature of the experiment (K), P is the barometric pressure (Torr), Δ is the correction to the reading of the barometer (Torr), and P_V is the vapor pressure (Torr) above the volumetric liquid at the temperature T [9]. The proposed technique was verified with different pure carbonates (Li_2CO_3, Na_2CO_3, and K_2CO_3) and with mixtures of these carbonates with an inert material (SiO_2). The relative error of the determination of CO_2 volume did not exceed 3%.

^{7}Li NMR spectra for $Li_7La_3Zr_2O_{12}$ and $Li_9La_3Zr_2O_{13}$ were recorded in the temperature range from −150 to 150 °C with a broad-line NMR spectrometer with a working frequency of 34 MHz.

The conductivity measurements were performed with pellets of LLZ powder; to form the pellets, LLZ was pressed under 100 MPa and was annealed at 1130 °C for 1 h. Both sides of the pellets were painted with gallium-silver electrode paste. The impedance measurements were performed in air at temperatures from 20 to 230 °C with an LCR-meter 819 (Goodwill Instruments) in the 0.012–100 kHz frequency range and with a two-probe cell with silver electrodes. The results were fitted with mathematical modeling. All of the conductivity measurements were performed on two sets of identical samples to assess the reproducibility of the results.

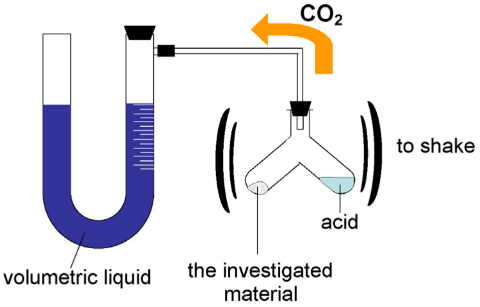

Fig. 1. The scheme of the cell to determine the amount of carbon dioxide liberated from the interaction of the investigated electrolyte with acid.

3. Results and discussion

3.1. The phase composition

The XRD patterns of $Li_xLa_3Zr_2O_{8.5+0.5x}$ ($x = 6–10$) are shown in Fig. 2. The indexing of the XRD patterns shows that the major peaks correspond to the tetragonal structure of LLZ; this structure has been described by many researchers, for example, [5]. According to XRD, $Li_6La_3Zr_2O_{11.5}$ also contains an impurity phase of lanthanum zirconate ($La_2Zr_2O_7$). It is likely that to maintain the tetragonal structure of LLZ, more alkali cations are needed relative to the zirconate anions; otherwise, the excess anions are released as lanthanum zirconate. The XRD patterns of $Li_{10}La_3Zr_2O_{13.5}$ show small peaks with an unidentified phase. Thus, the compound $Li_xLa_3Zr_2O_{8.5+0.5x}$ with lithium concentrations of $x = 7–9$ preserves the structure of tetragonal LLZ and does not decompose into several phases.

However, XRD analysis is not well suited for accurate determination of the phase composition of lithium compounds because the X-ray scattering from lithium atoms has low amplitude, especially against a background of heavy atoms, such as lanthanum. Neutron diffraction measurements are more suitable for such studies. Thus, for many lithium-containing garnets, the impurity of lithium carbonate was only detected by neutron diffraction studies. The lithium carbonate content in these systems ranged from 0.7 to 6 wt.% [12,13], although XRD analysis did not detect this impurity. Therefore, in the present study, we additionally used neutron diffraction to clarify the phase composition and the structural parameters of the synthesized solid electrolytes $Li_xLa_3Zr_2O_{8.5+0.5x}$ in the homogeneous region ($x = 7, 8, 9$).

Peaks from Li_2CO_3 are clearly observed in the neutron patterns (Fig. 3). The intensity of these peaks increases as the lithium content (x) increases. Based on neutronography, the concentrations of Li_2CO_3 in the samples $Li_xLa_3Zr_2O_{8.5+0.5x}$ are 0.5 (for $x = 7$), 2.9 ($x = 8$) and 4.2 ($x = 9$) wt. %, respectively. Thus, even within the "region of homogeneity" determined by XRD, the synthesized electrolytes do not have a single phase. Most likely, the synthesized

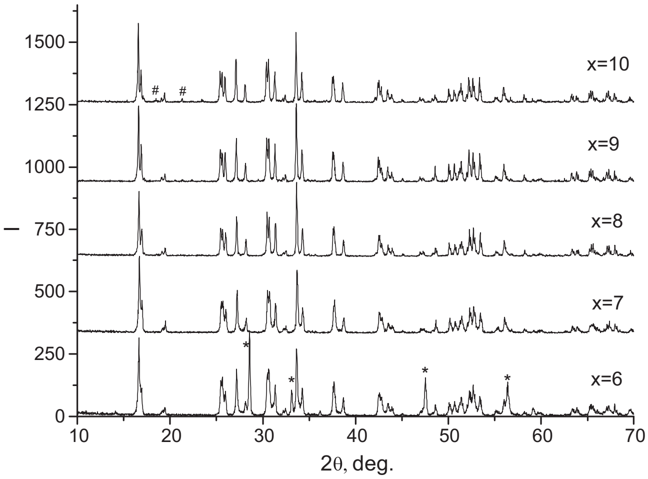

Fig. 2. XRD patterns of $Li_xLa_3Zr_2O_{8.5+0.5x}$ ($x = 6–10$). The peaks of impurities are marked as: * ($La_2Zr_2O_7$), # (unidentified).