REVIEW of official opponent
for the dissertation for the Doctor of Philosophy (Ph.D) in Chemical Sciences of Xu Xieyu on the topic: «Li-conductive ceramic electrolyte with NASICON structure for solid-state batteries», by specialty 1.4.15. Solid State Chemistry

Ph.D. thesis of Xu Xieyu is devoted to the problem of synthesis of fine powdered precursors for $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ by novel chemical methods, and also analysis of the influence of the background of obtained precursors on the sintering processes and the microstructure of $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ solid-state electrolyte samples, to issues of electrochemical testing and to the study of other functional and structural properties of such ceramic materials. Besides, a significant part of the work involves the development of numerical simulations by the phase field method to study the propagation process of dendritic structures of metallic lithium during battery charging. Without a doubt, the chosen direction of work is extremely relevant, high-demand and perhaps one of the most competitive fields in modern global science and engineering.

The goal of the work is the development of efficient approaches for obtaining ceramic solid-state electrolytes based on $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ phase composition with specified functional characteristics for solid-state secondary power supplies. I would like to note that the chosen goal of the work is a very labor-intensive and required the applicant to conduct extensive research. Special attention is given to comparing the results of the work with the current world level. Lithium Aluminum Titanium Phosphate (LATP) is a promising electrical material due to its high (electro)chemical and thermal stability, acceptable mechanical characteristics, low toxicity, relative cheapness and availability of initial (raw) substance. The work mainly studies the composition $x = 0.3$ due to its high ionic conductivity even at a room temperature.

The high practical significance of this work lies in the possibility of applying the results obtained by the author of this Ph.D. thesis to the development and production of highly effective lithium-conductive solid electrolytes for secondary power supplies. In particular, it has been clearly demonstrated that the combination of methodological developments by the author and his colleagues make it possible to obtain a ceramic solid electrolyte of composition $Li_{1,3}Al_{0,3}Ti_{1,7}(PO_4)_3$ with a high relative density of up to 96%, outstanding-high ionic conductivity of up to $\sim 8\times10^{-4}$ S/cm, elastic modulus of up to 125 GPa and a high hardness. One of the highlights is developed of a tape-casting method that makes it possible to produce a thin ceramic film of up to 60 microns in thickness after heat treatment. In addition, the applicant's proposal to use the amorphous glass phase of LATP as a sintering additive to produce high-density ceramics is novel and original.

The high reliability of the results and conclusions drawn is beyond doubt. The reliability of the experimental and theoretical results is ensured by the use of modern and appropriate instrumental and physicochemical methods, such as thermal analysis, high-temperature dilatometry, electron microscopy, X-ray phase analysis, Raman spectroscopy, nanoindentation, electrochemical testing, correct and rigorous use of numerical simulation, critical analysis of the results obtained, *etc*.

In my opinion, the main scientific results of the thesis are fully presented in 5 published scientific articles in international peer-reviewed journals. The results of the research were also shown at 4 specialized scientific conferences in 2022-2023.

The thesis consists of a brief introduction, an extensive and critical literature review, a detailed experimental part, the results and discussion, conclusions, references, acknowledgments and five chapters of Supporting information. The work is presented in a single volume of 234 pages and includes 148 figures, 24 tables, and 210 references.

Xu Xieyu's thesis are written in good scientific language, contain virtually no typos, the presentation of the material is generally dense and lapidary. The illustrative material has been carefully designed and is very clear. The content of the abstract fully corresponds to the thesis.

The main scientific conclusions presented in Xu Xieyu's thesis, which were submitted for defense, are original, have clear novelty. They are as follows:

1. It was established during modeling by the phase field method and visualization of the processes of lithium protrusions formation in the solid-state electrolyte that, with an overall fixed porosity, the presence of a large number of smaller diameter pores accelerates the process of electrolyte destruction during the growth of lithium protrusions. It was revealed that high values of grain boundary destruction energy suppress the propagation of lithium protrusions in the solid-state electrolyte, while the grain size factor makes a smaller contribution.
2. An original version method for the synthesis of $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ particles with the NASICON structure using polymerized matrices has been developed. It has been established that the concentration of reagents, as well as the process temperature are the main factors allowing to achieve a controlled average particle size in the range from 25 to 600 nm. The solid-state method makes it possible to obtain $Li1_{.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ particles with a controlled average size in the range from 300 to 2400 nm. The optimal sintering conditions for the resulting powders were determined, including sintering at 800 °C and 900 °C for 6 hours.
3. It has been demonstrated that the transition from a unimodal distribution of $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ particles to a bimodal distribution with 10 wt.% nano (~ 60 nm) and 90 wt.% submicron particles (~ 600 nm) makes it possible to obtain a ceramic solid state electrolyte with improved values of relative density of 96 ± 1 %, ionic conductivity of $(5.9 \pm 0.2)\times10^{-4}$ S/cm and elastic modulus of 119 ± 9 GPa compared to the values of relative density of 94 ± 1 %, ionic conductivity of $(4.8 \pm 0.5)\times10^{-4}$ S/cm and elastic modulus of 114 ± 9 GPa of ceramics made from the powder precursor without added nanoparticles.
4. A method for the producing of ceramic solid-state electrolyte using composites

based on crystalline and glassy phases of the $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ has been proposed. This approach makes it possible to avoid the process of abnormal grain growth during sintering and improve the functional properties of the solid-state electrolyte including increasing ionic conductivity up to $(7.8 \pm 0.2)\times10^{-4}$ S/cm, relative density up to 95.1 ± 0.3 % and elastic modulus up to 120 ± 8 GPa. The optimal mass ratio of the crystalline and glassy phases was established as 95 %:5 %. Based on the dilatometry data, a 2 steps sintering mode (570°C, 6 h; 900°C, 6 h) of composites based on $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ has been developed, which allows to achieve maximum ionic conductivity values of $(8 \pm 0.2)\times10^{-4}$ S/cm, relative density of 96.3 ± 0.2 % and elastic modulus of 125 ± 5 GPa.

5. An approach has been developed to forming synthesized powders in the form of thin membranes with the thickness from 60 to 250 μm. The approach is based on thin film tape casting of a photocurable multicomponent polymer mixture containing the target powder precursor of $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ followed by 2× stage heat treatment to remove polymer components and consolidate the ceramics. The proposed concept allows to assemble working prototypes of solid-state power supplies with improved specific characteristics by reducing the thickness of the solid-state electrolyte.
6. It has been shown that solid state electrolytes with both a bimodal particle distribution and ceramics obtained using glassy components demonstrate a high stability during electrochemical cycling of $Li||Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3||Li$ symmetric cells. The magnitude of the over voltage correlates with the ionic conductivity and relative density and is 121 mV for the solid-state electrolyte with bimodal particle distribution, and down to 100 mV for the ceramics based on glassy components, respectively. The prototype battery with Li metal anode and NCM111 cathode using the developed $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ solid state electrolyte demonstrated high performance characteristics: high cyclic stability over 100 cycles while maintaining a specific capacity of 79.1 % (100.3 mAh/g) at the discharge/charge rate of 0.1 mA/cm^2 in the voltage range of 3.0 - 4.2 V.

As comments to this work, I note the following:

1. In the experimental section, the composition and preparation method of highly loaded (up to 50 vol.%) photocurable paste(s) for the preparation of thin films by tape-casting are described briefly, without describing of key details.
2. In several places in the work, author notes the problem of «evaporation of lithium» during heat treatment of its compounds at temperatures above 1000 °C and the associated problem of the formation of harmful impurity phases. At the same time, for the synthesis of LATP glass phase at 1450 °C, stoichiometric amount of the initial precursors Li_2CO_3, Al_2O_3, TiO_2 and $NH_4H_2PO_4$ are proposed to be used. Has the author observed lithium losses in this process (or is this not significant)? In general, is the complex oxide with the composition $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ a phase with a variable lithium content?
3. Did the opponent understand correctly that the LATP hardness measured using the nanoindentation method and amounting to 4.6 ± 1.6 GPa applies only to thin ceramic films? Have other «classical» methods been used to study the hardness of bulk LATP ceramics? *In several sources, for instance, in J. Electrochem. Soc. 165, A1269 (2018) for dense ceramics, a similar value of microhardness is indicated according to the Vickers method at a load of 9.8 N. In the ref. Russ J. Electrochem. 57, 953 (2021) nanohardness was 4.5-5.8 GPa for LATP ceramics of lower density.* It would be beneficial to compare the author's results with those or other related refs.
4. However, one of the challenges in electrical engineering is ensuring the chemical and thermal compatibility of different functional and structural materials for the production of batteries. Were these aspects explored in the work? What limitations are imposed by the nature of LATP and the high anisotropy of its thermal expansion?
5. In the work, thin layer of platinum was deposed on the table of LATP to avoid contact with lithium metal. What is the reason for choosing platinum as a layer at the LATP/Li interface?
6. The work determined the ionic conductivity of all ceramic electrolyte samples, but there is no information according the electronic conductivity of LATP samples. At the same time, a polymerized matrices method was used to synthesize LATP nanoparticles. Did the author observe the influence of residual carbon on the surface of nanoparticles and its contribution to electronic conductivity and, as a consequence, to the results of electrochemical testing of cells?

These comments are not fundamental and do not affect the essence or main conclusions of the work. They also do not reduce the overall positive evaluation of the reviewed work.

Ph.D. thesis entitled «Li-conductive ceramic electrolyte with NASICON structure for solid-state batteries» fully meets the requirements established by the M.V. Lomonosov Moscow State University for this kind of works. The content of the dissertation corresponds to specialty 1.4.15. Solid State Chemistry (Chemical Sciences), namely the following directions:1) development and creation of methods for the synthesis of solid-phase compounds and materials; 2) establishment of «composition-structure-property» correlation for solid-phase compounds and materials; 3) study of the influence of synthesis conditions, chemical and phase composition, as well as temperature, pressure, irradiation and other external influences on the chemical and chemical-physical micro- and macroscopic properties of solid-phase compounds and materials, as well as the criteria defined in paragraphs. 2.1-2.5 Regulations on the awarding of academic degrees at the M.V. Lomonosov Moscow State University, and also drawn up in accordance with the requirements of the Regulations on the Council for the Defense of Dissertations for the Doctor of Philosophy (Ph.D) in Chemical Sciences, M.V. Lomonosov Moscow State University.

Thus, applicant Xu Xieyu deserves to be awarded the academic degree of Doctor of Philosophy (Ph.D) in Chemical Sciences in specialty 1.4.15. Solid State Chemistry.

Official opponent,
Doctor of Philosophy (Ph.D) in Chemical Sciences,
senior researcher of Kurchatov Chemical Research Complex (IREA) National Research Centre «Kurchatov institute».

Sokolov Petr Sergeevich ______________________________ 03 May 2024