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

Scientific research on the development of new materials for secondary power supplies is relevant and practically significant. One of the promising commercially available energy sources is lithium-ion batteries (LIB) due to their high specific energy density (240-270 Wh/kg) and power density (200-500 W/kg), long service life and stability during cycling. At the same time, a number of critical industrial, transportation, medical, telecommunications, information and engineering applications require achieving even higher performance. The possibility of significantly improving the main specific characteristics, as well as reducing costs, associated with the development of new electrode materials, as well as the use of new generations of materials based on solid-state electrolytes, which make it possible to achieve significant gains and improvements in specific energy, power and safety of devices today.

$Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ phase family solid-state electrolyte with NASICON structure has high ionic conductivity (up to 10^{-3} S/cm for monocrystal) at room temperature, low cost due to the absence of rare and trace elements in the compound, chemical stability in air, a wide window of operating voltage (2.8-4.8V relative to Li^+/Li), high mechanical strength (elastic modulus ~ 150 GPa), no toxic, high thermal stability up to ~ 1300°C. Methods for obtaining solid-state electrolytes based on LATP are divided into methods using solid state chemistry method, glass crystallization method, "soft chemistry" and chemical homogenization. Solid-state electrolyte ceramic samples have lower lithium-ion conductivity compared to the single crystal due to the negative contribution of grain boundaries and the presence of defects such as cracks and pores. Moreover, some types of defects in the ceramic electrolyte are sources of mechanical microstresses, which can lead to the formation of lithium protrusions during the electrochemical cycling of the battery and the risk of short circuit due to mechanical destruction of the electrolyte.

The relevance of the work is related to the development of new generations of materials for lithium-ion batteries with solid-state electrolytes, characterized by improved performance characteristics and safety. The feasibility of developing such materials is confirmed by the Decree of the President of Russia on the establishment of the State Program of the Russian Federation "Energy Development" and corresponds to the priority direction of the development of science, technology and engineering in the Russian Federation: Energy efficiency, energy saving, nuclear energy.

As part of Xu Xieyu's dissertation work, samples of Li-conducting ceramic electrolyte $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ with the NASICON structure were synthesized, and their structure and properties were studied. The PhD thesis consists of an abstract, literature review, experimental part, results and their discussion, conclusion, list of references and supporting information. The work is presented on 234 pages, contains 148 figures, 24 tables and 210 references to literary sources.

The results of the work are of great practical importance for the development and implementation of original approaches to obtain highly efficient lithium-conductive solid-state electrolyte for secondary power supplies. In particular, it has been demonstrated that the transition to a bimodal size distribution in an ensemble of ~ 600 nm submicron $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ particles with a fraction of 10 wt.% nano particles (~ 60 nm) makes it possible to obtain the ceramic solid-state electrolyte with improved values of relative density 96±1%, ionic conductivity $(5.9\pm0.2)\times10^{-4}$ S/cm and elastic modulus 119±9 GPa. A method for preparing the ceramic solid-state electrolyte using multi-component precursors based on crystal phase and the glass phase powders of $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ has been proposed. The approach used makes it possible to avoid the process of abnormal grain growth during sintering process and, as a result, to improve the functional properties of the solid-state electrolyte, including increasing the ionic conductivity up to $(7.8\pm0.2)\times10^{-4}$ S/cm, relative density up to 95.1±0.3% and elastic modulus up to 120±8 GPa. The optimal weight ratio of the crystalline and glass phases was established as 95:5 in the frame of this study. Based on dilatometry data, a two-step sintering mode (570°C, 6h; 900°C, 6h) of composites based on $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ was developed, which allows achieving maximum ionic conductivity values $(8\pm0.2)\times10^{-4}$ S/cm, relative density 96.3±0.2% and elastic modulus 125±5 GPa. Approaches have been developed to molding synthesized powders in the form of the solid-state electrolyte membrane with thickness down to 60 μm thick, which made it possible to assemble working prototypes of solid-state power supply with high performance characteristics.

Reliability of experimental results is confirmed by using an integrated approach depend on complementary physic-chemical methods, the reproducibility of the results obtained, as well as their agreement with literature data. To determine the phase composition and crystal structure - X-ray phase analysis (XRD), morphology - scanning electron microscopy (SEM), mechanical properties - nanoindentation and transport characteristics - impedance spectroscopy of the synthesized materials were used.

The main results obtained in Xu Xieyu's dissertation work are original and 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 $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ 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, respectively.

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 $(5.9\pm0.2)\times10^{-4}$ S/cm and elastic modulus of 119±9 GPa compared to the values of relative density of 94±1%, ionic conductivity of $(4.8\pm0.5)\times10^{-4}$ 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 $(7.8\pm0.2)\times10^{-4}$ 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, 6h; 900°C, 6h) 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 $(8\pm0.2)\times10^{-4}$ 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 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 overvoltage 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.

Xu Xieyu's dissertation work is written in good scientific language, is characterized by consistency, completeness and clarity of presentation and represents a completed, focused study. As comments to this dissertation, I note the following:

1. I noticed that Xu Xieyu did a lot of numerical simulations, and I would like to know whether the simulation results played a guiding role in the subsequent experimental work, or is it just a theoretical suggestion?
2. I noticed that Xu Xieyu emphasizes that the relative density of the solid-state electrolyte should be as high as possible, but the appropriate porosity in the solid material can help relieve the stress concentration in the material and delay the propagation of cracks. Or can solid-state electrolytes with appropriate porosity also perform well? Has the author investigated this by experiment or numerical simulation?
3. Can the mathematical model established by Xu Xieyu be applied to other application scenarios, such as the fatigue fracture process of ceramic materials under dynamic loads or the cracking and failure of ceramic materials caused by grain boundary corrosion?

These shortcomings are not fundamental and do not affect the essence and main conclusions of the work. Based on the dissertation results, 5 scientific works of the author have been published. The results of the work were presented at 4 international and Russian conferences. The content of the abstract fully corresponds to the dissertation. In general, Xu Xieyu's dissertation work, submitted for the degree of candidate of chemical sciences, is a completed scientific qualification work.

The dissertation 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", 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 Scientific Degree of Candidate of Sciences, M.V. Lomonosov Moscow State University.

Thus, applicant Xu Xieyu deserves to be awarded the academic degree of Candidate of Chemical Sciences in specialty 1.4.15 - Solid State Chemistry.

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