

REVIEW

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

Scientific research on the development of new materials for secondary power supplies is relevant and practically significant. $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ phase family solid-state electrolytes with NASICON structure have high ionic conductivity 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, high mechanical strength, no toxic effects, high thermal stability up to ~ 1300 °C. As part of Xu Xieyu's dissertation work, samples of Li-conducting ceramic electrolyte $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ with the NASICON structure were synthesized, and their structure and properties were studied. The relevance of Xu Xieyu's 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 author has developed practically useful new methods for the synthesis of powdered precursors to obtain $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ solid-state electrolyte with improved characteristics. Original methods for producing high-density NASICON structure $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ ceramic materials with high mechanical strength and ionic conductivity have also been proposed. A prototype battery with a Li metal anode and NCM111 cathode using the developed $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ electrolyte demonstrated high performance characteristics: high cyclic stability over 100 cycles while maintaining a specific capacity of 79 % (100 mAh/g) at a discharge/charge rate of 0.1 mA/cm² in the voltage range of 3.0-4.2 V. The results of the work are of fundamental and practical importance for the development and implementation of original approaches to obtaining highly efficient lithium-conducting electrolytes for secondary power supplies.

The scientific novelty and relevance of the results obtained is beyond doubt. The author synthesized the samples and characterized them by the necessary physico-chemical methods to establish the phase composition, microstructure, ion transport, mechanical properties, and electrochemical characteristics of the battery prototype. I would also like to note that in addition to the experimental work, the author carried out modeling using the phase field method of the formation of lithium protrusions in a solid-state electrolyte depending on the grain size, their mechanical properties and pore morphology, which made it possible to predict the optimal properties of ceramics to reduce the negative consequences of the growth of dendritic structures of metallic lithium. The obtained theoretical and experimental results were analyzed and interpreted in detail by the author. Based on the dissertation materials, 5 scientific works of the author have been published. The results of the work were presented at 4 international and local conferences.

Xu Xieyu's Ph.D. abstract is written in competent scientific language, the logic of presentation is consistent, the illustrative material is deeply developed and visually formidable. As comments that arose while reading the Ph.D. abstract, I would like to

note the following:

1. There is no data about the electronic conductivity of the obtained $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ samples. At the same time, the presence of electronic conductivity due to partial remained carbon or reduced titanium in the electrolyte significantly affects the process of formation of lithium protrusions and, therefore, the process of electrolyte degradation.
2. Temperature affects the transport of lithium ions of solid-state electrolyte ceramic materials. At what temperature has the author measured the ionic conductivity of the solid-state electrolyte? Did the author carry out measurements at different temperatures to estimate activation energy of the obtained electrolytes?
3. The author deposited nanoscale platinum on the surface of the solid-state electrolyte to protect it. Has the author considered using other functional interfaces at the boundary between lithium and electrolyte to provide both efficient electron and ion transport during the lithium cycling process of the battery?

The work « Li-conductive ceramic electrolyte with NASICON structure for solid- state batteries» meets the requirements established by the M. V. Lomonosov Moscow State University for this kind of works. The content of the work 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 of 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.

Therefore, the 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.

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ПОДПИСЬ РУКИ
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АДМИНИСТРАТИВНОГО ОТДЕЛА
М.А. ГУСЕВА




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