Effect of doping with cations and anionic groups on the ionic conductivity properties of latp solid electrolytes for li-ion batteries

Yelnury Baltash[1*], A. Mashekova[1,2], M. Yegamkulov[1,2], I. Trussov[1], A. Mukanova[1,2 **]
[1]*Institute of Batteries, Z05P4X0, Kazakhstan, Nur-Sultan,53, Kabanbay Batyr Avenue*
[2]*Nazarbayev University, Z05P4X0, Kazakhstan, Nur-Sultan,53, Kabanbay Batyr Avenue*
*E-mail: 97.elnura@gmail.com , **E-mail: aliya.mukanova@nu.edu.kz

The good energy capacity of lithium-ion batteries (LIBs) makes them promising electrochemical energy storage devices. Existing commercial batteries use flammable liquid electrolytes, which are unsafe, toxic and environmentally unsound, and have poor chemical stability. Recently, solid Li-ion conducting ceramic electrolytes have received considerable attention, since they combine high ionic conductivity with low electrical conductivity, chemical stability and potentially sufficient mechanical properties. Currently, Al-substituted lithium titanophosphate $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ is the most common solid electrolyte with a NASICON structure for use in solid-state electrochemical devices due to its high ionic conductivity (~10^{-3}-10^{-4} S/cm at room temperature), thermal stability, stability in air, relatively inexpensive synthesis and safety. It is known that the ionic conductivity of NASICON materials is significantly affected by the microstructure (porosity, grain size, presence of impurity phases), and the conductivity strongly depends on the sample density. However, LATP has the disadvantage that occurs at contact with lithium metal where Ti^{4+} is reduced to Ti^{3+}, leading to degradation of electrolyte surface and reduction of its ionic conductivity. This work proposes doping LATP with tetravalent, divalent cations and anionic groups as to suppress titanium reduction. The polycationic doping of LATP was carried out by adding a various amount of Zr, Hf ,Ca, Mg, Sr and SiO_4^-, MoO_4 in LATP structure. The synthesis of doped LATP with cations and anionic groups was performed by molten flux, solid-state reaction and solution-based methods. The samples were synthesized and their structural, morphological characteristics and ionic conductivity properties were studied. X-ray analysis revealed the introduction of divalent cations into the LATP structure without the formation of impurity phases. Doping of LATP with calcium, magnesium and strontium decreased the total ionic conductivity by an order of magnitude. The results of this work clearly demonstrate that there is possibility of forming a NASICON-structured material with higher Li reduction resistance due to lower Ti content, and also provides an opportunity to develop solid electrolytes with different compositions.

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