

LI DISTRIBUTION IN THE IONIC CONDUCTOR $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ WITH $0 \leq x \leq 0.6$ STUDIED BY NEUTRON DIFFRACTION

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$\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}\text{P}_3\text{O}_{12}$ (LTP) is among the most widely investigated solid electrolyte materials for Li ion batteries because of its relatively high ionic conductivity, chemical stability and mechanical strength. Its ionic conductivity is induced by partial substitution of Ti with Al, in combination with the incorporation of additional Li ions into the structure. The electrical conductivity therefore depends strongly on the substitution parameter x . A series of $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ powders with $0 \leq x \leq 0.6$ were prepared by two different syntheses routes, a) solid state reaction and b) a novel sol-gel method leading to high phase purity, densification activity and conductivity. The highest ionic conductivity of $1.0 \times 10^{-3} \text{ S cm}^{-1}$ at 25°C was obtained for $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ti}_{1.5}(\text{PO}_4)_3$ with nearly theoretical density.

We have studied the distribution of Li ions in this series by neutron diffraction analysis at different temperatures. The refinements revealed that excess Li ions are scattered throughout the crystal structure at temperatures above 600 K, making it difficult to precisely determine Li positions and non-stoichiometry. At low temperatures Li ions may occupy a set of different positions, namely the 6a site identified in our previous study or the 18e and 36f sites discussed in the literature [1-3]. A correlation between the synthesis method and the location of Li ions was observed, which is consistent with the ionic conductivity of these materials.

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