

# Study of Amorphous $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ as Solid Electrolyte Material and Its Applications in All-Solid-State Li-ion Batteries



**Yubin Zhang**

**WPI, Materials Science & Engineering**

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## Abstract

Lithium ion batteries have been widely used in portable electronic devices, electric vehicles, and grid storage because of their high energy density, high power density and long cycle life. However, safety is one of the intrinsic issues of current lithium ion batteries with flammable liquid electrolyte. Therefore, All-solid-state Li-ion batteries (ASSLiB) attract lots of attention mainly due to their higher safety compared to commercial Li-ion batteries. Among all the candidates of solid electrolyte materials, amorphous  $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$  (LLTO) shows promising ionic conductivity and electrochemical stability.

In this work, we successfully synthesize both amorphous LLTO thin film and powder by sol-gel process. The ionic conductivity, which is a critical parameter for solid electrolyte, increases from  $2.32 \times 10^{-8}$  S/cm to  $9.01 \times 10^{-6}$  S/cm with the control of annealing time. Accordingly, the morphology of the thin film changes, and solvent evaporation, surface refinement and crystallization phases occur sequentially. It also indicates that there is an optimal synthesis condition for the LLTO film. In order to further increase the ionic conductivity to meet the requirements of ASSLiB, Strontium (Sr) is introduced as dopant and the ionic conductivity further reaches  $8.38 \times 10^{-5}$  S/cm at 30 °C with 5% of Sr doping, which is about one order of magnitude higher than that of undoped LLTO. It is also confirmed that amorphous  $\text{Li}_{0.35}\text{La}_{0.5}\text{Sr}_{0.05}\text{TiO}_3$  (LLSTO) is stable in direct contact with lithium and with electrochemical stability window up to 10V.

Thiophosphate-based electrolytes also have shown great promises because of their high ionic conductivity ( $\sim 2 \times 10^{-3}$  S/cm). However, the narrow operation voltage and poor compatibility with high voltage cathode materials impede their application in the development of high energy ASSLiB. With a facile wet chemical approach, a thin layer of amorphous LLSTO with 15-20 nm was coated at the interface between NMC and  $\text{Li}_6\text{PS}_5\text{Cl}$ . Attributed to the high stability of  $\text{Li}_6\text{PS}_5\text{Cl}$  with NMC/LLSTO and outstanding ionic conductivity of the LLSTO interfacial coating and  $\text{Li}_6\text{PS}_5\text{Cl}$ , the electrochemical stability window of  $\text{Li}_6\text{PS}_5\text{Cl}$  was greatly improved to 4.0 V (vs. Li-In). At room temperature, the fabricated ASSLiB exhibits outstanding capacity of 107 mAh/g and keeps stable for 850 cycles with a high capacity retention of 91.5 % at C/3. Inspired by this interfacial modification, we further investigated the solid electrolyte system with NMC 811, the high Nickel cathode material. A layer of LiOH on NMC 811 was generated simultaneously with cathode sintering. With an optimized thickness, NMC 811 was protected from  $\text{Li}_6\text{PS}_5\text{Cl}$ . The LiOH-NMC811 cathode material exhibit outstanding coulombic efficiency (>99%), excellent cyclability (130 mAh/g for 600 cycles) and satisfactory rate capability (119.4 mAh/g at 1C).