Grain boundary atomic structures in solid-state electrolyte Li$_{0.28}$La$_{0.53}$TiO$_3$

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Lithium ion rechargeable battery has been developed to meet the requirements as power sources for electric or hybrid vehicles. Present lithium-ion battery compose of cathode, anode and liquid organic electrolytes, which have several disadvantages for safety issues such as leakage, corrosion to the interface of the electrode. Inorganic solid electrolyte has a potential to solve these problems because of its high thermal and electrochemical stability. To develop the alternative all solid-state lithium-ion lithium secondary batteries, the inorganic solid electrolytes with high Li ion conductivity is required.

The conductivity in solid electrolyte is typically less than one tenth or hundredth of that in liquid materials. Li$_{3x}$La$_{(2/3)-x}$□$_{(1/3)-2x}$TiO$_3$ (LLTO) is well known solid-state electrolyte having very high ionic conductivity at room temperature. The conductivity in a single crystal reaches up to 1.1x10$^{-3}$ S·cm$^{-1}$ (x ~ 0.11), which is high enough to be used as a practical electrolyte [1]. However, polycrystalline LLTO contains a large number of grain boundaries, which potentially decrease the ionic conductivity. In this study, we investigate the local atomic structure including grain boundary using atomic-resolution scanning transmission electron microscopy (STEM), which is powerful for identifying the relationship between the atomic structure and ionic conductivity.

LLTO has a double perovskite-type structure, and it is composed of the alternative La-rich and La-poor (or Li-rich) layers along the c-axis. These layers are filled by TiO6 octahedrons. Owing to such layered structure, it has been reported that Li ion can diffuse in the La-poor two-dimensional layers. [2] Figure 1(a), (b) show atomic-resolution ADF and ABF-STEM images obtained from LLTO (x ~ 0.11). The right-hand side of these images is aligned along the [100] direction, and it can be clearly seen alternative stacking of La-rich and La-poor layers by Z-contrast image. In the La-poor layers, one can see some bright dotted contrast, suggesting that some of atomic column has high La concentration. Moreover, 90° domains can be seen, which also possibly decrease local ionic conductivity [3]. At the grain boundary region, there are no secondary precipitates or amorphous phases. Detailed discussion will be given in this presentation.

References
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FIG. 1 (a), (b) Simultaneously recorded HAADF and ABF-STEM images obtained from grain boundary area of LLTO, where the right region is viewed along the [100] direction. The scale bar is 5 nm.