Atomic structure of a grain boundary in $LiMn_2O_4$ thin film and its influence on battery properties

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All solid-state Li-ion batteries is a one of potential alternative for conventional Li-ion batteries containing flammable liquid electrolytes for applications as power sources for electric vehicles. For this purpose, Spinel structure $LiMn_2O_4$ has been considered one of the most promising cathode materials because it is lower in cost and has lower toxicity than many other candidates, including the conventional cathode material, $LiCoO_2$, while still maintaining a high rate capability, high energy density, high voltage and good safety performance. Especially, its high rate, high Li ion conduction due to three-dimensional Li ion conduction path compare with other two-dimensional $LiCoO_2$, one-dimensional Olivine structure allows us flexibility of battery design (orientation). In this all-solid thin film structure, presence and its influence of grain boundary can be a critical problem. However its importance, detailed structure and its influence on battery properties has not been reported yet. Therefore, in this study, we tried to analyze structure and its influence on battery properties of grain boundary in $LiMn_2O_4$ thin-film using atomic scale structure analysis using Cs-corrected STEM and theoretical calculations. $LiMn_2O_4$ thin-film by Chemical Solution Deposition (CSD) methods on (La,Li)NbO_3 substrate. By STEM observation, in our $LiMn_2O_4$ thin-film, an 180° twist boundary with (111) boundary plane was often found in vicinity of the interface between $LiMn_2O_4$ and substrate. Our calculation revealed ever though coherent boundary structure with small boundary energy of 0.25 J/m^2, battery voltage was dropped by 0.2 to 0.7 V. Even more, not only battery voltage but also Li conduction was seriously affected by this grain boundary. The activation energy of Li migration significantly increased from 0.4-0.7 eV to 3.25eV. This indicates this grain boundary should act as a blocking layer of Li migration.

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