Modification of Grain-Boundary for Prevention of Lithium Growth through Garnet-type Solid Electrolytes

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Garnet-based lithium ion conducting solid electrolyte is a promising solid electrolyte for all solid-state batteries [1]. However, lithium dendrite growth during lithium deposition on the negative electrode causes short-circuit with increasing current density [2, 3]. In this work, we prepared garnet-based $Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$ (LLZT) pellets, with different synthesis conditions, and investigated correlation between the pellet structure and short-circuit prevention.

LLZT powder and pellets were prepared using a solid-state reaction and spark plasma sintering technique, respectively, as reported in our previous work [2]. The prepared pellets are designated as LLZT-air (conventional method), LLZT-w/o-air (without exposing to air), and LLZT-2calc (calcined twice with addition of LiOH). A combination of structural and chemical characterization techniques, such as SEM, STEM and FT-IR revealed presence of LiOH and Li_2CO_3 on the LLZT powder and effects of excessive lithium salt on the microstructure of the pellets. To investigate the short-circuit prevention, symmetric cells of Li | LLZT | Li were cycled at various current densities at 25°C, which were gradually increased until the cells showed voltage drop [2, 3]. As shown in Figure 1, the critical current density, at which voltage drop occurred, depended on the specimens. LLZT-2calc exhibited the highest, while LLZT prepared without exposing to air showed low short-circuit prevention. This suggests that Li_2CO_3 and/or LiOH on surface of starting LLZT powder is effective to improve density of grain boundaries in the pellets to suppress the short circuit.

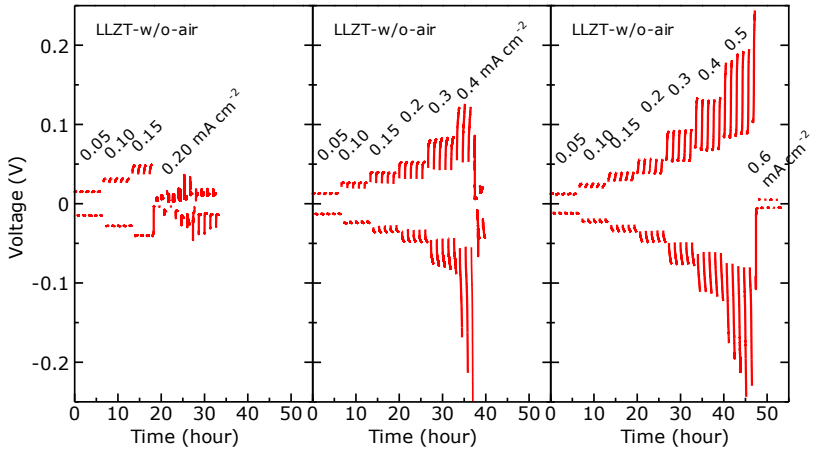

Figure 1. DC polarization curves of Li | LLZT | Li cells using LLZT pellets prepared with different condition.

References:

[1] R. Murugan, V. Thangadurai, W. Weppner, *Angew. Chem. Int. Ed.* 46 (2007) 7778-7781.

[2] R. Hongahally Basappa, T. Ito, H. Yamada, *J. Electrochem. Soc.* 164 (2017) A666-A671.

[3] R. Hongahally Basappa, T. Ito, T. Morimura, R. Bekarevich, K. Mitsuishi, H. Yamada, *J. Power Sources* 363 (2017) 145-152.