Li plating/stripping behavior of Al-doped $Li_7La_3Zr_2O_{12}$ ceramics with different grain size

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Garnet-structured $Li_7La_3Zr_2O_{12}$ (LLZ) is a promising candidate as a solid electrolyte for all-solid-state lithium batteries because of its high Li^+ ion conductivity [1], high mechanical strength [2], and chemical stability against metallic Li [3]. LLZ has been partially substituted with various elements to improve its characteristics. Al-substituted cubic LLZ ceramics with a relative density of 90% or more show a high conductivity of over 10^{-4} S cm^{-1}at 25ºC. However, the reported values of conduction activation energy range from 25 to 40 kJ mol^{-1} [4,5]. This variety of activation energies is presumed to be based on the difference in microstructure of the sintered bodies. Moreover, the microstructural difference influences the Li plating/stripping behavior. Cheng *et al.* examined Li/LLZ/Li symmetric cells using LLZ ceramics with different grain size [6]. The cell using LLZ with smaller grains in the range of 20 to 40 μm showed higher galvanostatic cycling stability than that with larger grains in the range of 100 to 200 μm. A sintered body composed of much smaller grains of LLZ can improve the cycling stability, but has not been studied. In this study, two LLZ ceramics with different grain size were prepared to investigate the relationship between their grain sizes and ion conducting properties. Furthermore, lithium symmetric cells using their ceramics with smaller grains than that reported previously were fabricated and both galvanostatic cycling stabilities were compared.

Two types of LLZ powders, which had different particle size distribution and almost the same composition, were pressed at 120 MPa and sintered at 1230ºC for 20 h in air. The surfaces of the sintered bodies were conditioned by an automated polisher using a diamond polishing paste. Both samples showed high relative densities of more than 94%, but grain sizes were quite different. One had a larger grain size of 5~20 μm (LLZ_LG) and the other had a smaller grain size of mainly less than 1 μm (LLZ_SG). The LLZ_LG showed the total conductivity of 3.6×10^{-4} S cm^{-1} at 25ºC and the activation energy of 32 kJ mol^{-1}. On the other hand, the LLZ_SG showed 4.4×10^{-4} S cm^{-1} and 26 kJ mol^{-1}. Li symmetric cells were fabricated by sandwiching the LLZ ceramics with Li foils and applying an isostatic pressure of 100 MPa. Galvanostatic cycling tests were carried out at 100ºC for 2 h in half a cycle. The cell using LLZ_SG was stably cycled under a high current density of 1.0 mA cm^{-2} without short-circuiting, while the cell using LLZ_LG showed an unstable potential at a lower current density. Therefore, the grain-growth-suppressed LLZ ceramic exhibited the higher room-temperature conductivity, the lower activation energy and the better cycling performance of Li plating/stripping.

References:

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