Lithium Dissolution/Deposition Behavior of Al-Doped Li$_7$La$_3$Zr$_2$O$_{12}$ Ceramics with Different Grain Sizes

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Lithium dissolution/depocitiation behavior of Al-doped Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZ) was investigated in terms of grain size of LLZ-sintered bodies. One LLZ had smaller grain sizes of primarily less than 1 μm (LLZ_SG), and the other had larger grain sizes of 5–20 μm (LLZ_LG). The total resistance of a Li symmetric cell using LLZ_SG was smaller than that using LLZ_LG at 100 °C. The cell using LLZ_SG was stably cycled at 100 °C without short-circuiting at a high current density of 1.3 mA cm$^{-2}$, while the cell using LLZ_LG was stably cycled at current densities below 0.26 mA cm$^{-2}$. Stronger bonding at grain boundaries for LLZ_SG was expected to contribute to the improvement of cyclability.

Conventional lithium-ion batteries based on organic liquid electrolytes have been widely studied, but their safety is still a concern. Conversely, all-solid-state lithium batteries based on solid electrolyte have attracted attention for their high energy density and chemical stability against molten lithium. Garnet-type Li-ion conductor Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZ) is believed to be a promising candidate as a solid electrolyte because of its high conductivity and chemical stability against molten lithium. High lithium metal has a high theoretical specific capacity (3861 mAh g$^{-1}$) and low redox potential (~3.045 V vs. SHE). Higher battery energy density is expected by the use of lithium metal anode. However, it is known that lithium dendrite penetrates liquid electrolyte. The use of solid electrolyte has been proposed as a solution to this problem. Monroe et al. have suggested that Li dendrite should be suppressed if the shear modulus of solid electrolytes is more than twice that of metallic Li (~3.4 GPa). In the case of all-solid-state cells, it is expected that dense inorganic electrolytes with a high shear modulus can prevent the Li growth. Although LLZ, with a high shear modulus of ~60 GPa, was applied as a solid electrolyte, Li penetrated LLZ, resulting in short-circuiting. Therefore, there must be another factor that affects Li penetration besides the shear modulus. However, the factors remain unclear. It is considered that high LLZ/Li interfacial resistance leads to detrimental current focusing due to inhomogeneous current distributions, causing rapid initiation of lithium growth at interfaces. Various attempts have been conducted to reduce the interfacial resistance. For example, Tsai et al. have used a thin buffer layer of Au to improve the contact between LLZ and Li. Compared with the Li/LLZ interfacial resistance without Au buffer, the interfacial resistance dramatically decreased because of the formation of Li-Au alloys, resulting in good cycling stability. Similar phenomena have been reported by using Li alloys. On the other hand, Cheng et al. examined the influence of grain size of a sintered body on Li/LLZ interfacial resistance and cycling stability of Li symmetric cells. They prepared two types of sintered bodies; one was composed on Li/LLZ interfacial resistance and cycling stability of Li symmetric cells. They suggested that the difference in LLZ/Li interfacial resistances is attributed to the difference in grain sizes, which impacted the cycling stability. However, the investigation of the relationship between grain size and cycle performance in a region of much smaller grain size has not been studied. Very recently, we have investigated the relationship between grain size and conductivity using LLZ ceramics with much smaller grains than the previously reported LLZ. We prepared two sintered bodies with different grain sizes; one had a larger grain size of 5–20 μm (LLZ_LG), and the other had smaller grain size of ≤1 μm (LLZ_SG); LLZ_SG exhibited higher ion conductivity than LLZ_LG.

In this study, the influence of grain size on Li/LLZ interfacial resistance and cycling stability was examined by using both LLZ_LG and LLZ_SG sintered bodies. Li symmetric cells using these sintered bodies were fabricated and galvanostatic cycling tests were conducted. After the cycling tests, the microstructures of the ceramics were analyzed.

Experimental

Two Al-doped LLZ powders with different particle sizes (DLZ-2 and Improved LLZ 2, Daiichi Kigenso Kagaku Kogyo Co., LTD.) were ball-milled for 45 min. The milled powders were pressed into pellets (diameter = 10 mm) under a pressure of 60 MPa. Further, the pellets were isostatically cold-pressed under a pressure of 120 MPa. These green bodies were sintered at 1230 °C for 20 h, covered with mother powders of the same composition. X-ray diffraction measurements (XRD, SmartLab; Rigaku Corp.) were performed with CuKα radiation. X-ray photoelectron spectroscopy (XPS) (Thermo Fisher SCIENTIFIC) of the LLZ surfaces was performed with an Al-Kα source (1486.6 eV). The observed binding energies were calibrated with the adventitious C 1s peak at 284.7 eV.

Symmetric Li/LLZ/Li cells were fabricated by sandwiching lithium metal foils of thickness 0.25 mm and stainless steel foils (current collector). To ensure good contact between metallic Li and LLZ, the cells were isostatically cold-pressed under a pressure of 100 MPa for 10 min. Alternating current (AC) impedance spectroscopy (Solartron SI-1260) was performed with an amplitude of 10 mV in the frequency range from 10$^7$ Hz to 0.1 Hz. For the Li dissolution/deposition experiment, square waves of current were applied to the cells at 100 °C using charge-discharge measuring devices (BTS-2004, Nagano Corp.). The current density was stepwise increased from 0.078 to 1.9 mA cm$^{-2}$ after every group of ten cycles for 1 h and ten cycles for 2 hours. Scanning electron microscopy (SEM, SU8220, Hitachi Ltd.) observations were conducted at an acceleration voltage of 1.0 kV for the cross-section of the cycled cells.
Results and Discussion

Figure 1a shows the XRD patterns of LLZ_LG and LLZ_SG sintered bodies. Si powder was used as an external standard. No peaks of impurity phases were observed in either sintered body, indicating that pure cubic-LLZ was obtained. These grain sizes were estimated from the SEM images of thermally etched surfaces of each sintered body as shown in Figs. 1b and 1c: LLZ_LG had a larger grain size of 5–20 μm than LLZ_SG (grain size of ≤ 1 μm). It is known that LLZ reacts with H2O to produce LiOH, followed by reaction with CO2 to form Li2CO3.18,19 Although the reaction layer is very thin, it is enough to dramatically increase the interfacial resistance and degrade cycling stability.20,21 Hence, it is extremely important to remove Li2CO3 layers from the surfaces of the LLZ sintered bodies. In this work, LLZ surfaces were first conditioned with an automated polisher and dry-polished using a sand paper with grit number 3000 in an Ar glove box. There would be thus no difference in the surface conditions between LLZ_LG and LLZ_SG. On the other hand, Rtotal was so small at 100 °C that for LLZ_SG has remained unclear. Both surfaces of LLZ_LG and LLZ_SG were pretreated in the exact same manner; they were first conditioned with an automated polisher and dry-polished using a sand paper with grit number 3000 in an Ar glove box. There would be thus no difference in the surface conditions between LLZ_LG and LLZ_SG. On the other hand, Rtotal was so small at 100 °C that resistance components could not be separated. Rtotal of the cell using LLZ_SG was much smaller than that using LLZ_LG. The difference in Rtotal at 100 °C as well as that at 25 °C is determined by the difference in Rinterface.

Galvanostatic cycling tests for the Li/LLZ/Li cells were conducted at 100 °C. Figure 4a shows the result of the test for Li/LLZ/Li and its enlarged one is shown in Figure 4b. The voltage profile of the cell was stable at current densities less than 0.26 mA cm−2. In contrast, it gradually increased and suddenly dropped to ~0 V at a current density of 0.39 mA cm−2. Figure 4c shows the results of Li dissolution/deposition behavior of the cell using LLZ_SG, and its enlarged one is shown in Figure 4d. It was stably cycled at a high current density of 1.3 mA cm−2 for 2 hours, corresponding to an areal capacity of 2.6 mA h cm−2. Yonemoto et al. also conducted a Li dissolution/deposition test at 100 °C.27 Li films with a thickness of 2.0 μm were plated and stripped at a current density of 0.1 mA cm−2 (0.41 mA h cm−2). Compared with this result, the cell with LLZ_SG...
showed better cyclability even at high current densities. It showed variable overpotential and sudden potential drop at a current density of 1.9 mA cm\(^{-2}\). This behavior indicated failure of the cell. The difference in these cycling stabilities should be related to the difference in the interfacial resistances at Li/LLZ, as mentioned in Figure 3.

Figures 5a and 5c show the cross-sectional SEM images of the cells using LLZ\_LG and LLZ\_SG, respectively, after short-circuiting. Figures 5b and 5d show enlarged images of Figures 5a and 5c, respectively. A web-like structure was observed on the cross section of LLZ\_LG. The diameter of one cell in the web-like structure was estimated to be 5–20 μm, which is similar to the grain size of LLZ\_LG. Considering that Li grows through grain boundaries easily, the web-like structure is probably composed of metallic Li.\(^{28,29}\) On the other hand, a web-like structure was not observed on the cross section of LLZ\_SG, suggesting that Li growth was suppressed. It is reported that Li penetrates through interconnected pores and grain boundaries.\(^{26}\) Li probably deposited in those areas for LLZ\_SG after short-circuiting, but a trace of Li penetration was not observed in Fig. 5c because the areas were a quite minor region. Li growth, therefore, depends on the difference in the microstructure of the grain boundary. Recently, various attempts have been conducted to reduce the interfacial resistance between LLZ and Li by inserting Au buffer layers, because it is assumed that large interfacial resistance influences Li growth. In addition, physically preventing the Li growth is also effective. We have reported that LLZ\_SG had stronger bonding at grain boundaries than LLZ\_LG,\(^{17}\) suggesting that Li growth would be avoided by enhancing the bonding at grain boundaries in LLZ electrolytes.

In this study, we prepared LLZ ceramics with much smaller grains than that reported by Cheng et al.\(^{12}\) LLZ ceramic with smaller grains had stronger bonding at grain boundaries than that with larger grains. Li barely grew through the LLZ with smaller grains, resulting in good cycling stability.

Conclusions

LLZ ceramics with different grain sizes were applied to Li symmetric cells, and the relationship between grain size and cycling stability was investigated. Galvanostatic cycling tests were conducted at 100°C. The cell using LLZ\_SG with submicron grains had a smaller interfacial resistance than the cell of LLZ\_LG with 5–20 μm grains. LLZ\_SG was more stably cycled than LLZ\_LG. A web-like structure consisting of dendritic Li was observed on the cross section of LLZ\_LG after short-circuiting. In contrast, the morphology of the cross section of LLZ\_SG was not changed by cycling, suggesting that the use of LLZ\_SG with stronger bonding at grain boundaries is effective in preventing the Li penetration. We believe that these results lead to further understanding and improvement of all-solid-state lithium batteries with a lithium metal negative electrode.
Figure 5. SEM images of the cells after short-circuiting using (a) LLZ_LG, (b) enlarged SEM image of the boxed area in (a), (c) LLZ_SG, and (d) enlarged SEM image of the boxed area in (c).

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