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Compatibility of Li₇La₃Zr₂O₁₂ Solid Electrolyte to All-Solid-State Battery Using Li Metal Anode

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Electrochemical properties of $\text{Li}_7\text{La}_3\text{Zr}_2O_{12}$ (LLZ) were investigated to reveal its availability as a solid electrolyte for all-solidstate rechargeable batteries with a Li metal anode. After calcination at 1230°C, a well-sintered LLZ pellet with a garnet-like structure was obtained, and its conductivity was 1.8×10^{-4} S cm⁻¹ at room temperature. The cyclic voltammogram of the Li/LLZ/Li cell showed that the dissolution and deposition reactions of lithium occurred reversibly without any reaction with LLZ. This indicates that a Li metal anode can be applied for an LLZ system. A full cell composed of a LiCoO₂/LLZ/Li configuration was also operated successfully at expected voltage estimated from the redox potential of Li metal and LiCoO₂. Simultaneously, an irreversible behavior was observed at the first discharge and charge cycle due to an interfacial problem between LiCoO₂ and LLZ. The discharge capacity of the full cell was 15 μ A h cm⁻². These results reveal that LLZ is available for all-solid-state lithium batteries.

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All-solid-state lithium batteries consisting of solid electrodes and a Li-ion conductive solid electrolyte have been expected to overcome the safety problem of present lithium-ion batteries including flammable nonaqueous solvent.¹ High lithium-ion conductivity, low electronic conductivity, and good chemical stability against electrode materials are required for electrolytes in rechargeable lithiumion batteries.² Lithium-ion conductivity of ceramic electrolytes is lower than those of nonaqueous electrolytes, but some oxides, for example, $Li_{0.35}La_{0.55}TiO_3~(LLT)^{3-5}$ and $LiTi_2(PO_4)_3~(LTP)$,^{6,7} possess high ionic conductivities of $\sim 10^{-3}$ to 10^{-4} S cm⁻¹, which are acceptable for an all-solid-state battery. Therefore, many research groups have investigated their applications to all-solid-state rechargeable lithium-ion batteries. However, anode materials with a lower redox potential than 1.8 V vs Li/Li⁺ cannot be utilized in an LLT and LTP system due to the redox reaction of titanium, which limits the energy and power densities of all-solid-state rechargeable lithium-ion batteries.

In the past several years, a series of garnet-like structural compounds with a nominal chemical composition of Li₅La₃M₂O₁₂ (M = Nb, Ta) has been investigated as a novel family of fast lithium-ion conductors by Thangadurai and co-workers.⁹ These compounds contain La³⁺ and M⁵⁺ in the cubic and octahedral environments of the garnet structure. Recently, Li₇La₃Zr₂O₁₂ (LLZ) also has been synthesized by Murugan et al. as a new garnet-like compound with lithium-ion conductivity.¹⁰ This material has received much attention as a ceramic electrolyte due to its chemical stability against lithium metal and relatively high lithium-ion conductivity (3 \times 10⁻⁴ S cm⁻¹). However, the electrochemical properties of LLZ have hardly been investigated. In this study, we examined the electrochemical properties of LLZ minutely to reveal its availability as a solid electrolyte in all-solid-state rechargeable lithium-ion batteries.

Experimental

LLZ was prepared by a solid-state method according to the procedure reported elsewhere.¹⁰ The powders of Li₂CO₃, La₂O₃, and ZrO₂ were used as starting materials. They were mixed and ballmilled with zirconia balls ($\phi = 0.2 \text{ mm}$) for 6 h in 2-propanol. 10 wt % excess of Li₂CO₃ was added to compensate the loss of lithium during heat-treatments, resulting in the molar ratio of Li:La:Zr = 7.7:3:2 in the starting mixture. The milling process was repeated after each heat-treatment in air (first, at 900°C for 6 h and second, at 1125°C for 6 h). The obtained powder was finally pressed into a pellet under 50 MPa for 5 min and then annealed at 1230°C for 36 h in air at a heating rate of 1°C min⁻¹. The crystal structure of LLZ was confirmed by X-ray diffractometer (XRD, Rigaku RINT-UltimaII) using Cu K α radiation after each heat-treatment. The morphology of the LLZ pellet was observed with a scanning electron microscope (SEM, JEOL).

Both surfaces of the LLZ pellet after heat-treatment were polished to obtain flat surfaces and to control its thickness before electrochemical measurements. The conductivity of LLZ was measured by the ac impedance method using an SI 1260 impedance/gainphase analyzer (Solartron Analytical) in the frequency range from 10 Hz to 1 MHz and an alternating voltage signal of 10 mV. In this measurement, Au was sputtered on each surface of the LLZ pellet to ensure electrical contact between the Cu current collector and the LLZ pellet. A symmetric cell with a Li/LLZ/Li configuration was constructed and evaluated by cyclic voltammetry and chronopotentiometry using ALS-660B (BAS Inc.). Cu foils were used as current collectors. The cell was heated at 140°C for 1 h to obtain better contact between the LLZ pellet and the Li foil.

A LiCoO₂ cathode was prepared on the LLZ pellet by the sol–gel method.¹¹ The precursor sol for LiCoO₂ was prepared from CH₃COOLi, Co(CH₃COO)₂·4H₂O, *i*-C₃H₇OH, CH₃COOH, and H₂O (molar ratio = 1.1:1:20:10:70) according to a previous paper.¹² 50 μ L of precursor sol was dropped on the LLZ pellet. Then, the pellet was calcinated at 450°C for 15 min. This procedure was repeated two times to obtain thick LiCoO₂ film. Finally, the pellet was calcined at 800°C for 1 h. A Li metal anode was prepared by the same procedure as that of the Li/LLZ/Li cell. A galvanostatic charge and discharge test of the LiCoO₂/LLZ/Li cell was performed by using a battery charge/discharge unit (HJ1001SM8A, Hokuto Denko) under a constant current density of 2 μ A cm⁻², and cutoff voltages were 2.5 and 4.3 V for discharge and charge, respectively.

Results

The XRD patterns for LLZ obtained after each heat-treatment are displayed in Fig. 1. The structure of LLZ was not cubic at 900°C, and it turned to a cubic phase after heat-treatment at 1230°C. The peak intensity of the XRD patterns increased with heat-treatment temperature. The diffraction peaks observed after heat-treatment at 1230°C were assigned to a well-crystallized garnet-like structure, as previously reported by Thangadurai et al.⁹ and Murugan et al.¹⁰ The formation of pyrochlore La₂Zr₂O₇ as an impurity phase was also

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Figure 1. XRD pattern of LLZ powder calcined at (a) 900 and (b) $1125^{\circ}C$ and pellet calcined at (c) $1230^{\circ}C$.

confirmed on the XRD patterns of the LLZ powder sintered at lower than 1125°C (Fig. 1a and b). After heat-treatment at 1230°C, the diffraction peaks derived from the impurity disappeared, suggesting that the LLZ pellet prepared in this study had a single phase of Li₇La₃Zr₂O₁₂ with a garnet-like structure. Figure 2 shows typical cross-sectional SEM images of the LLZ pellet. The pellet was sintered well and grain boundary was not observed. Some voids existed in the cross-sectional view, but it can be confirmed that they were isolated sufficiently to prevent electrical short-circuit in rechargeable lithium batteries. It is expected that the void formation can be reduced by using smaller LLZ particles for the pellet preparation. An impedance spectrum of the prepared LLZ pellet measured at room temperature is exhibited in Fig. 3. Clear semicircles were not observed; only a line with slope of 45° appeared, probably due to almost no grain-boundary resistance. The obtained impedance spectrum was not consistent with that reported by Murugan et al., which showed a nearly vertical tail at the low frequency range.¹⁰ This difference may be attributed to the starting materials. They used LiOH as a Li source and La_2O_3 after drying at 900°C as a La source. Meanwhile, Li₂CO₃ and La₂O₃ without any treatment were used in this research. This difference may cause the different impedance behavior. The conductivity of LLZ was calculated to be 1.8 $\times 10^{-4}$ S cm⁻¹ at room temperature by using an apparent thickness (0.1 cm) and surface area (0.5 cm^2) of the pellet.

To investigate the potential use of the lithium metal as anode for all-solid-state rechargeable batteries with an LLZ electrolyte, cyclic voltammetry and chronopotentiometry were carried out by using the electrochemical cell with a Li/LLZ/Li configuration. Figure 4 reveals the cyclic voltammogram (CV) taken at 10 mV min⁻¹. The dissolution and deposition reactions of lithium were observed reversibly, indicating that lithium-ion could be transferred through the



Figure 2. Cross-sectional SEM image of LLZ pellet calcined at 1230°C.



Figure 3. Impedance spectrum of the prepared LLZ pellet measured at room temperature in the frequency range of 0.1–1 MHz.

LLZ electrolyte without degradation of LLZ. The chronopotentiograms of the Li/LLZ/Li cell obtained under different current densities from 10 to 50 μ A cm⁻² are depicted in Fig. 5. The overpotentials for the dissolution and deposition reactions of lithium increased with current density. The time–potential curves for the lithium dissolution and deposition collected at the same current density showed the same absolute overvoltage. Up to 10 μ A cm⁻², the dissolution and deposition curves gave the mirrored relationship at least until 600 s. This behavior also suggests that the lithium dissolution and deposition took place reversibly.





Figure 4. CV of Li/LLZ/Li cell at room temperature taken at 10 mV min⁻¹.

Figure 5. (Color online) Chronopotentiograms of Li/LLZ/Li cell obtained under different current densities from 10 to 50 μ A cm⁻².



Figure 6. XRD pattern of LiCoO₂ cathode prepared on LLZ pellet.

The LiCoO₂ cathode was prepared on the LLZ pellet by the sol-gel method. Figure 6 shows the XRD pattern of the LiCoO₂ cathode on the LLZ pellet. Diffraction peaks attributed to LiCoO₂ were observed clearly, indicating that the LiCoO₂ cathode was prepared successfully. All of the diffraction peaks were assigned to LiCoO₂ or LLZ, and no impurity phase was observed. The thickness and weight of the LiCoO₂ cathode were 6 μ m and 12 mg, respectively. Figure 7 reveals the galvanostatic charge and discharge curves of the LiCoO₂/LLZ/Li cell. The cell worked successfully at the expected operation voltage estimated from the redox potential of the Li metal and LiCoO₂. A large irreversible capacity was observed, and the discharge capacity of the all-solid-state cell was 15 μ A h cm⁻².

Discussion

The electrochemical properties of the LLZ solid electrolyte were investigated to confirm its compatibility with all-solid-state rechargeable Li batteries with a Li metal anode. The well-sintered LLZ pellet was obtained by calcination at high temperature as well as at 1230°C. The pellet was sintered well and grain boundary could not be found. The conductivity of the pellet was relatively high $(1.8 \times 10^{-4} \text{ S cm}^{-1})$, which is acceptable for an all-solid-state battery.

The CV of the Li/LLZ/Li cell revealed that the dissolution and deposition reactions of lithium occurred reversibly without side reactions with LLZ. This result indicates that the Li metal anode can be applied for the LLZ system. Although the CV was measured only at the first cycle, it was confirmed that the LLZ pellet was stable against contact with a large excess of molten lithium for 72 h. The Li/LLZ interface is thought to be stable for some period. However, a long time stability of the LLZ against the Li metal is not clear at the moment. The chronopotentiograms of the Li/LLZ/Li cell showed the mirrored relationship. However, the mirrored relationship collapsed over 10 μ A cm⁻². A resistance of the cell estimated from the chro-



Figure 7. Galvanostatic charge and discharge curves of LiCoO_2/LLZ/Li cell measured at 2 $\,\mu A$ cm^{-2}.



Figure 8. Impedance spectrum of $LiCoO_2/LLZ/Li$ cell measured at room temperature in the frequency range of 0.1–1 MHz.

nopotentiograms was ca. 5500 Ω , which is much higher than that of the LLZ pellet (1100 Ω). This difference may be due to the large interfacial resistance between the LLZ pellet and lithium metal, derived from an inhomogeneous current distribution. Therefore, thin and dense LLZ electrolyte with a uniform surface is needed for operation under higher current densities. The increment in the contact area between LLZ and lithium metal is also one of the solutions to reduce the internal resistance of the cell. We have reported that a solid electrolyte with a three-dimensionally ordered macroporous (3DOM) structure, which possesses a large surface area, is very useful to cause a decline in the internal resistance.^{13,14} Therefore, using LLZ with a 3DOM structure, cell operation under a higher current density would become possible.

The LiCoO2/LLZ/Li cell demonstrated clearly reversible charge and discharge behavior, indicating that an all-solid-state battery with a lithium metal anode and a LiCoO₂ cathode can be fabricated by using an LLZ solid electrolyte. However, the discharge capacity was only 15 μ A h cm⁻². This was only 0.2% of the full capacity $(8.4 \text{ mA h cm}^{-2})$ estimated from the weight of the cathode material. This low capacity is attributed to the high interfacial resistance between the LLZ pellet and electrodes, as shown in the impedance spectrum of the LiCoO₂/LLZ/Li cell (Fig. 8). A large semicircle was observed in Fig. 8. This semicircle did not appear in the impedance spectrum of the LLZ pellet. Therefore, the semicircle is attributed to the interfacial resistance between the LLZ pellet and the electrode. The resistance of the Li/LLZ/Li cell estimated from the chronopotentiograms was ca. 5500 Ω , but the impedance of the semicircle was much larger, nearly 1 M Ω . Therefore, most of the contribution of the semicircle may be the interfacial resistance between the LiCoO₂ cathode and LLZ. The XRD pattern of LiCoO₂/LLZ displayed no impurity formation (Fig. 6). However, a small amount and/or amorphous impurity may be formed at the interface and provide high resistance to the cell. Optimization of the preparation process for the LiCoO₂ cathode on LLZ and screening of a more suitable cathode are needed.

These results proved that LLZ has a very high potential to produce all-solid-state lithium batteries with high power and energy densities. However, some studies such as long time stability and rate capability of the LiCoO₂/LLZ/Li cell as well as the Li/LLZ/Li are needed. These tests are under way, and it will be reported in due course.

Conclusions

The electrochemical properties of LLZ solid electrolyte were investigated for application to all-solid-state lithium batteries using a lithium metal anode. The LLZ pellet prepared in this study was chemically and electrochemically stable against lithium metal. Accordingly, the cell with a Li/LLZ/Li configuration was successfully operated. Moreover, in the LiCoO₂/LLZ/Li cell, reversible charge

and discharge behavior was observed, indicating that the all-solidstate battery with lithium metal anode was operated successfully. These results revealed that LLZ is available for all-solid-state lithium batteries with high power and energy densities. However, the discharge capacity of the LiCoO2/LLZ/Li cell was only 15 μ A h cm⁻². Further study to reduce interfacial resistance is required.

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