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Short communication

Electrochemical properties of $Li_7La_3Zr_2O_{12}$ solid electrolyte prepared in argon atmosphere

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ABSTRACT

A sintered bulk $Li_7La_3Zr_2O_{12}$ (LLZ) pellet was prepared in Ar flow. The Li ion conductivity of LLZ pellet sintered in Ar flow was lower than that sintered in air due to mainly high grain boundary resistance, indicating that air promotes sintering of LLZ. On the other hand, stability against molten Li metal was not affected by sintering atmosphere. $LiCoO_2$ was prepared by a sol–gel method and no impurity phase was observed by XRD identification. All-solid-state battery with Li/LLZ/$LiCoO_2$ configuration was constructed and operated successfully.

1. Introduction

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 non-aqueous solvent [1]. $Li_{0.35}La_{0.55}TiO_3$ (LLT) [2–4] and $LiTi_2(PO_4)_3$ (LTP) [5,6] possess high ionic conductivities of 10^{-3} to 10^{-4} S cm^{-1}, which are acceptable for the all-solid-state battery. Therefore, many research groups have investigated their applications to all-solid-state rechargeable lithium-ion batteries. However, electrochemical window of LLT and LTP electrolyte is limited by facile reduction of Ti^{4+} and this provides restrict application of them because the narrow electrochemical window conducts to low energy and power densities of batteries. A solid electrolyte with high lithium-ion conductivity, low electronic conductivity, and wide electrochemical window is strongly required for the all-solid-state battery.

In the last several years, a series of garnet-like structural compounds have been investigated as a novel family of fast lithium ion conductors by Weppner and co-workers [7–10]. Among them, $Li_5La_3Ta_2O_{12}$ (LLTa) and $Li_7La_3Zr_2O_{12}$ (LLZ) have been paid much attention because of their stable nature against Li metal [7,10].

Application of LLZ electrolyte to the all-solid-state battery has been attempted in some groups including us and some new findings has been reported [11,12]. One of the serious problems of LLZ is very difficult to obtain sintered bulk LLZ because of easy formation of the pyrochlore $La_2Zr_2O_7$ (LZ). In fact, we have confirmed a formation of the LZ phase in Al_2O_3-added LLZ pellet sintered at 1100 °C in air [13]. In order to prevent LZ formation, Kokal et al. has attempted preparation of LLZ at low temperature using sol–gel method [14]. On the other hand, Kumazaki et al. reported incorporation of Si and Al was very effective to reduce grain boundary resistance of LLZ [15]. Therefore, study on sintering behaviour of LLZ is worthwhile work. The sintering process in all reports [10–15] has been performed in air so far. The sintering in inert atmosphere has been reported yet.

In this paper, we prepared sintered bulk LLZ under Ar flow. Electrochemical properties of the sintered LLZ and compatibility with the all-solid-state battery using Li metal anode were examined.

2. Experimental

$Li_7La_3Zr_2O_{12}$ (LLZ) was prepared by a solid-state reaction according to our previous paper [13]. LiOH (Kanto Kagaku) $La(OH)_3$ (Shinetsu kagaku) and ZrO_2 (TOHSO) were mixed in agate mortar and then calcined at 900 °C for 6 h. γ-Al_2O_3 (Daimei Kagaku) was added to the obtained LLZ powder as a sintering additive. The Al_2O_3-added powder was pelletized into a pellet with 13 mm diameter and then sintered at 1000 °C for 36 h under Ar flow of 100 ml min^{-1}. After sintering, the pellets were polished to obtain flat surface and to control its thickness to 1 mm. An observation of cross section of the pellet was performed by scanning electron microscope (SEM, JEOL). XRD (RINT-Ultima, Rigaku) was used for identification of crystal phases of the pellet using Cu K_α radiation.

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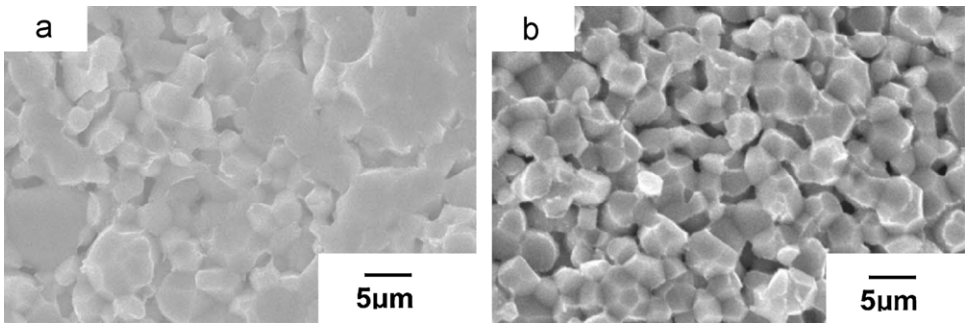

Fig. 1. A cross-sectional SEM image of LLZ pellet sintered at 1000 °C for 36 h in (a) air and (b) Ar flow.

Li ion conductivity of the LLZ pellet was examined by the AC impedance method with SI1260 impedance/gain-phase analyzer (Solartron analytical). Prior to measure, Au was sputtered on both sides of the pellet to ensure electrical contact. Data was collected at ±5 mV voltage signal in a frequency range of 1 kHz to 1 MHz.

Stability of the pellet against molten Li metal was tested by a contact of the pellet with molten Li on Ni plate in Ar-filled globe box. After contact for 72 h, the pellet was removed from the molten Li and supplied for XRD measurement.

$LiCoO_2$ cathode was prepared on the pellet by a sol–gel method. A mixture of $LiCoO_2$ powder (Celceed 10N, Nippon Chemical Industrial Co. Ltd.) and its precursor sol composed of CH_3COOLi, $Co(CH_3COO)_2{\cdot}4H_2O$, i-C_3H_7OH, CH_3COOH, H_2O, and poly-vinylpyrrolidone (molar ratio = 1.1:1:20:10:70:1) was impregnated onto the LLZ pellet and then calcined at 700 °C for 2 h [16]. A thickness of the cathode was about 10 μm (ca. 1 mg). The impregnated $LiCoO_2$ was characterized by XRD and Raman spectrum (NRS-1000, JASCO) with 532 nm laser radiation. The all-solid-state battery with Li/LLZ/$LiCoO_2$ configuration was fabricated by putting Li metal on bare side of $LiCoO_2$/LLZ pellet. The cyclic voltammetry (CV) of the all-solid-state battery was measured at scan rate of 1 mV min^{-1} with scan range of 3.0–4.2 V vs. Li/Li^+ at room temperature.

3. Results

Fig. 1 displays a cross-sectional SEM image of LLZ pellet sintered at 1000 °C for 36 h in Ar flow and air. Many grains with facets were observed in Ar flow sample. These many grains make us image that the pellet possesses high grain boundary resistance derived by much number of grain boundaries. The LLZ pellet sintered in air was sintered better than in Ar flow. In the LLZ pellet sintered in air, some grains fused each other and formed a large grain [13]. The densities of LLZ pellet sintered in Ar flow and air were 4.3 and 4.6 g cm^{-3}, respectively. The molar ratio of Li:La:Zr estimated by ICP was 6.7:3.0:2 and 6.8:3.1:2 in air and Ar calcination, respectively.

XRD pattern of LLZ pellet sintered at 1000 °C for 36 h in Ar flow was depicted in Fig. 2. The XRD patterns were well-matched with the standard pattern known as a garnet phase $Li_5La_3Nb_2O_{12}$ (PDF 45-0109), indicating that LLZ with garnet-like structure was prepared [10]. No diffraction peak assigned to impurity phase was observed.

A complex impedance plot of the LLZ pellet using blocking Au electrodes is revealed in Fig. 3. A semicircle and Warburg-type impedance were appeared at high frequency and low frequency regions, respectively. This tail at low frequencies corresponds to a usual behaviour of ionically blocking electrodes with ionically conductive nature [15]. A similar behaviour has been observed another garnet-like ceramic conductor [17–20]. σ_{bulk} and σ_{total} estimated from intercepts of the semicircle at high and low frequency sides were 1.1×10^{-4} and 4×10^{-5} S cm^{-1}, respectively. These are lower than LLZ pellet sintered in air in our previous report ($\sigma_{bulk} = 2.4 \times 10^{-4}$ and $\sigma_{total} = 1.4 \times 10^{-4}$ S cm^{-1}) [13].

In order to test a stability of the LLZ against Li metal, the LLZ pellet was put on melting Li metal for 72 h. No visual change of the LLZ pellet was confirmed before and after contact with Li metal. XRD patterns of them were also completely identical and new diffraction peaks did not appear (Fig. 4), indicating that the LLZ was stable against Li metal.

All-solid-state battery with Li metal anode using LLZ solid electrolyte was fabricated by using $LiCoO_2$ cathode. The $LiCoO_2$ cathode with about 10 μm thickness on the LLZ was prepared by sol–gel method. XRD pattern showed clear diffraction peaks of $LiCoO_2$ (Fig. 5). All other peaks were attributed to LLZ and no impurity phase was detected. In Raman spectrum (Fig. 6), clear Raman bands were confirmed at 489 and 598 cm^{-1}. These bands are attributed to E_g and A_{1g} Raman active modes, respectively, of HT (high temperature)-$LiCoO_2$ with hexagonal layered structure [21] which is favourable structure for cathode of lithium battery [22].

All-solid-state battery composed of Li/LLZ/$LiCoO_2$ configuration was fabricated by setting Li metal on bare side of $LiCoO_2$/LLZ pellet and was supplied to CV measurement. Obtained cyclic voltammogram is shown in Fig. 7. A clear redox couple was observed and the redox behaviour was stable during first 10 cycles. It is concluded that the all-solid-state battery with Li metal anode is operated successfully by using the LLZ electrolyte sintered in Ar flow.

Electrochemical properties of LLZ pellet sintered in Ar flow and its compatibility with all-solid-state battery using Li metal anode were examined. The LLZ pellet sintered in Ar flow contained numerous grains and more grain boundaries were observed than the pellet

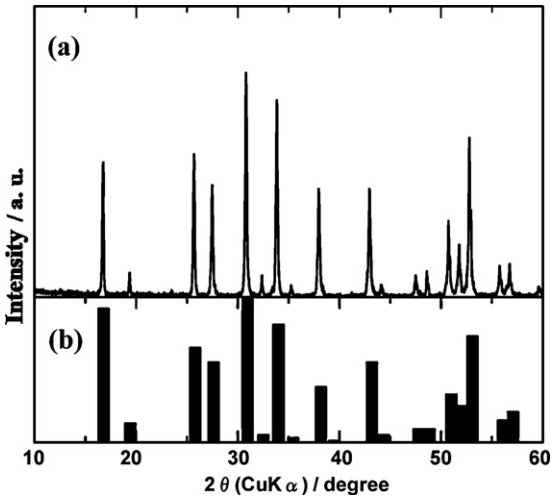

Fig. 2. XRD patterns of LLZ pellet sintered at 1000 °C for 36 h in Ar flow. (a) LLZ pellet sintered in Ar flow and (b) standard pattern of a garnet phase $Li_5La_3Nb_2O_{12}$ (PDF 45-0109).

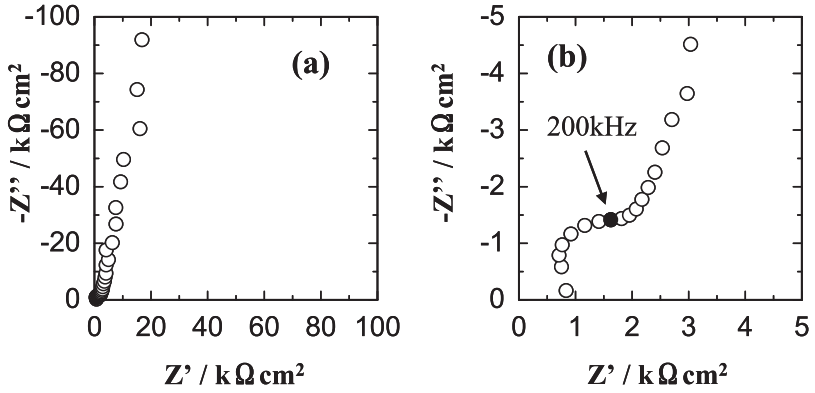

Fig. 3. Complex impedance plot of LLZ pellet sintered at 1000 °C for 36 h in Ar flow. (a) Whole plot and (b) magnified plot around origin.

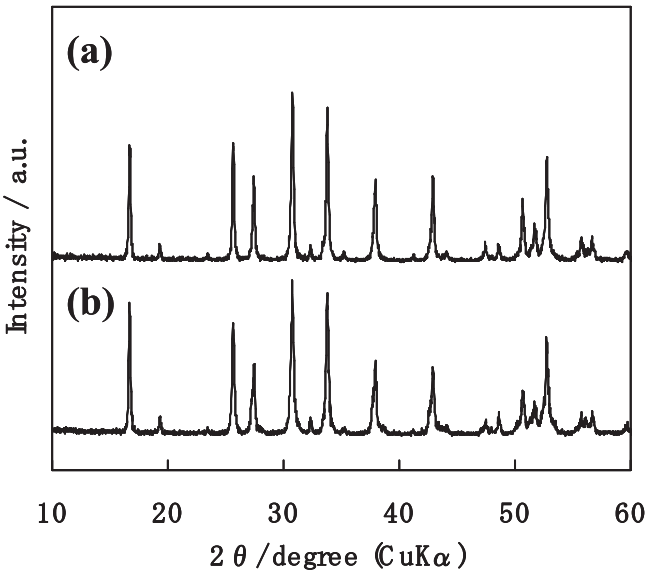

Fig. 4. XRD patterns of LLZ pellet sintered at 1000 °C for 36 h in Ar flow. (a) After and (b) before contact with molten Li metal for 72 h.

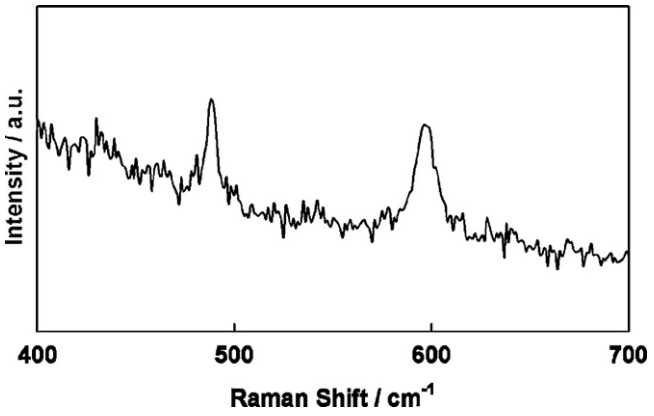

Fig. 6. Raman spectrum of LLZ pellet after $LiCoO_2$ impregnation.

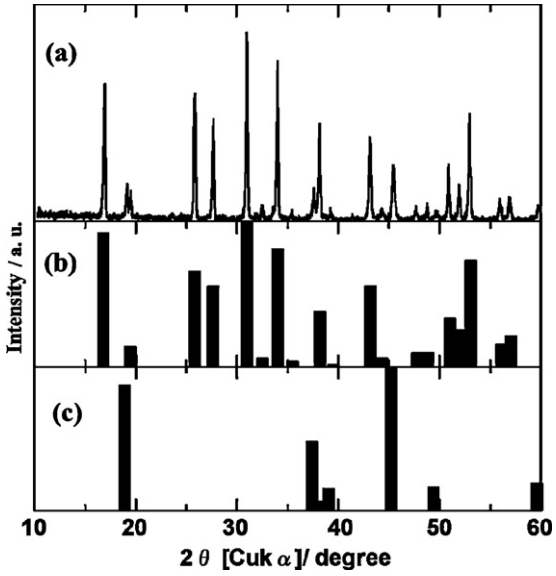

Fig. 5. XRD patterns of (a) LLZ pellet after $LiCoO_2$ impregnation, (b) standard pattern of a garnet phase $Li_5La_3Nb_2O_{12}$ (PDF 45-0109) and (c) standard pattern of $LiCoO_2$ (PDF 50-0653).

sintered in air. It is inferred that air (oxygen and/or moisture in air) promotes sintering of LLZ and produces well-sintered pellet, leading to low grain boundary resistance. A small amount of impurity, which cannot be detected by XRD, may be produced and contribute to increase of grain boundary. However, the contribution is thought to be small because completely different morphologies depending on the sintering condition were observed in the SEM images. The

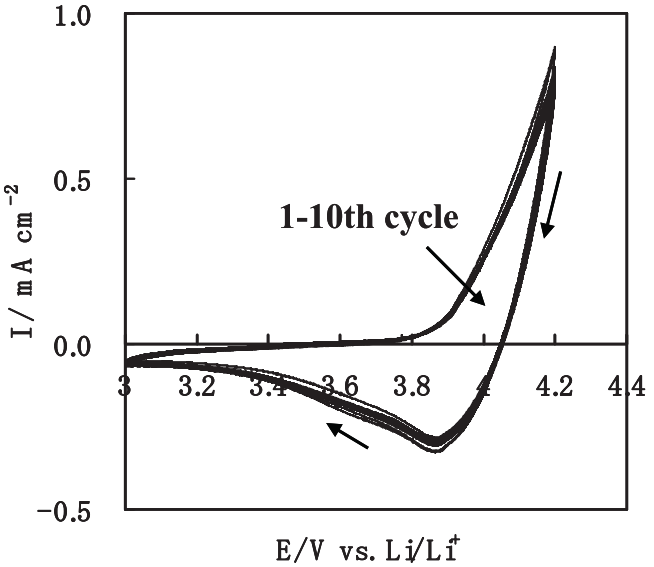

Fig. 7. Cyclic voltammogram of Li/LLZ/$LiCoO_2$ cell at scan rate of 1 mV min^{-1} and scan range of 3.0–4.2 V vs. Li/Li^+.

reason of low bulk conductivity of LLZ pellet sintered in Ar has not been cleared yet. On the other hand, stability against molten Li metal was not affected by sintering atmosphere, both pellets did not react with molten Li metal. It is concluded that fabrication of all-solid-state battery using LLZ sintered in Ar flow is possible.

4. Conclusions

A sintered bulk LLZ pellet was prepared under Ar flow. And its electrochemical properties and compatibility with the all-solid-state battery using Li metal anode were examined. The LLZ pellet sintered in Ar flow contained numerous grains and more grain boundaries were observed than the pellet sintered in air. It is speculated that air promotes sintering of LLZ and conducts to lower grain boundary resistance of the LLZ pellet. On the other hand, stability against molten Li metal was not affected by sintering atmosphere, both pellets sintered in air and Ar did not react with molten Li metal. It is concluded that LLZ sintered in Ar flow can be applied to all-solid-state battery with Li metal anode.

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