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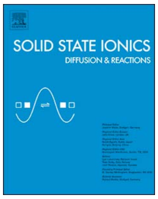

Quasi-solid-state lithium batteries using bulk-size transparent $Li_7La_3Zr_2O_{12}$ electrolytes

Shoichi Sugata[a], Noriko Saito[a], Akio Watanabe[a], Ken Watanabe[a], Je-Deok Kim[a], Kan Kitagawa[b], Yosuke Suzuki[b], Itaru Honma[a,c,*]

[a] *NIMS Open Innovation Center, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan*
[b] *DENSO CORPORATION, 500-1 Minamiyama, Komenoki-cho, Nisshin, Aichi 470-0111, Japan*
[c] *Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan*

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ABSTRACT

A thick bulk-sized $Li_7La_3Zr_2O_{12}$ (LLZ) solid electrolyte is successfully prepared using a polymer complex method and a hot isostatic pressing (HIP) treatment. Despite the difficulties of densification, HIP-treated LLZ can be prepared as a transparent ceramic pellet because of its ~200 μm primary grain size, and its conductivity is improved by its increased density ($>$ 99%). An all-solid-state lithium battery is fabricated by using a mixed conducting ionic liquid gel to connect the bulk-sized LLZ electrolyte and a $LiFePO_4$ (LFP) cathode. The introduction of the mixed conducting gel layer reduces the electrode/electrolyte interface resistance. The specific discharge capacity of the active cathode material is 169 mAh g^{-1} (current density of 0.046 mA cm^{-2}), which suggests that almost the full capacity of LFP can be utilized even under the all-solid-state cell design. The coulombic efficiency (ηc) is ≈1, and no side reactions are observed. The LFP/LLZ/Li cell shows a high electrochemical stability against the Li metal anode, and the cell operates for 20 cycles without dendrite growth causing a short circuit under a charge current density of 0.591 mA cm^{-2} (1/2 C rate).

1. Introduction

Li-ion batteries are widely used in electric devices, but they suffer from serious problems, such as leaking electrolytes and fire hazards. In contrast, all-solid-state Li-ion batteries (ASS-LIBs) use solid electrolytes; thus, these batteries do not leak and are non-flammable [1–3].

Li metal is one of the most suitable anode materials for high energy density Li-ion batteries because of its high theoretical capacity and low reaction potential. Various anode materials are known, but the high redox potentials of anode materials other than Li lower the operating voltage of these batteries. Despite their advantages, Li metal anodes have some associated safety and cyclability concerns [4]. The growth of Li dendrites in liquid electrolytes can cause an internal short circuit of the batteries, possibly resulting in fire and explosion [5,6]. The use of solid electrolytes as separators in ASS-LIBs is expected to suppress dendrite growth.

The Li ion conductivity of solid electrolytes is lower than that of liquid electrolytes; however, various solid electrolytes with relatively high Li-ion conductivities have been reported [7–9]. Among them, solid oxide electrolytes have some advantages, such as safety and chemical stability against gaseous components in the atmosphere. $Li_{0.35}La_{0.55}TiO_3$ and $LiTi_2(PO_4)_3$ possess high ionic conductivities (10^{-3} to 10^{-4} S cm^{-1}) [10–14], and their applications in ASS-LIBs have been extensively investigated. However, Li metal cannot be used as the anode material because Ti reacts with Li [15]. This instability restricts the choice of anode materials. Some oxide electrolytes are stable against Li metal, such as lithium phosphorus oxynitride (LiPON) [16], but their Li-ion conductivities are not sufficiently high.

Weppner et al. reported a series of garnet-type oxides with high Li ionic conductivities [17–19]. Among them, $Li_7La_3Zr_2O_{12}$ (LLZ) is a promising electrolyte for ASS-LIBs because of its high Li ion conductivity (5×10^{-4} S cm^{-1}), stability to the Li metal anode, and wide potential window [19]. The Li ion conductivity of LLZ depends on its crystal structure and microstructure [19–23]. Cubic-phase LLZ shows a conductivity that is two orders of magnitude higher than that of tetragonal-phase LLZ, and Al_2O_3 addition can stabilize the cubic structure [22].

While the application of LLZ to ASS-LIBs has been investigated by several research groups [24–29], the power density of bulk-type batteries using an LLZ electrolyte is insufficient for practical use because of Li dendrite growth at high current densities. One effective approach for the suppression of Li dendrite growth is densification of the LLZ

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[*] Corresponding author at: Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan.
E-mail address: i.honma@tagen.tohoku.ac.jp (I. Honma).

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electrolyte. A high sintering temperature of approximately 1230 °C is needed to obtain dense LLZ ceramics (relative density of 96%), which are produced from the precursor synthesized in the solid-state reaction [30]. The sintering temperature is so high that the Li ions in LLZ are vaporized. The use of hot pressing (98% at 1000 °C) and spark plasma sintering (99.8% at 1150 °C) to obtain a high sintered density at a relatively low temperature has been reported [22,31], and hot isostatic pressing (HIP) is another method for densifying LLZ ceramics [32–34]. In HIP treatment, the pellet is isostatically pressed under a high gas pressure, which suppresses vaporization of the constituents and removes the closed pores. A sintered LLZ pellet can be further densified by HIP treatment, and the highly densified transparent LLZ sample exhibits suppressed Li dendrite growth [35]. In ref. 35, the inhomogeneous LLZ sample have transparent parts and opaque parts in the pellet after HIP treatment, and it was confirmed experimentally that Li dendrite growth were suppressed in the transparent part. The homogeneousness of the pellet before HIP treatment is important for the densification and the suppression of Li dendrite growth. We chose the polymer complex method (PCM) to prepare homogeneous LLZ. PCM was invented by Pechini and has been applied in the preparation of many oxide powders [36,37]. PCM includes a combined process of metal complex formation and in situ polymerization. Then, the prepared polymer is calcined to produce the desired oxide, and the components are homogeneously dispersed. Other advantages of PCM include small particle size, second phase suppression, and low heat treatment temperature [38,39]. These characteristics allow a highly homogeneous sintered LLZ pellet with few impurities to be obtained.

The resistivity of the electrode/electrolyte interface in a solid-state battery presents further problems, and it is difficult to form a good ion-conducting path at the solid/solid electrode/electrolyte interface, especially in bulk solid-state batteries. Therefore, we expect that the interfacial resistance could be decreased by using a soft material as the cathode. We used ionic liquid (IL) to prepare a soft cathode material, since the high conductivity, wide potential window, low vapor pressure, and non-flammability of ILs make them promising high-performance electrolyte materials [40–42]. Based on these properties, ILs have been investigated as new electrolytes for use in Li-ion batteries [42–44], and have also been reported to stabilize oxide surfaces [45–47]. Composite materials containing ILs and oxide materials can be handled as quasi-solids or gels because of the strong interactions between the IL and the oxide, and these soft materials were show similar transport properties to bulk ILs [48].

In this research, a highly densified and homogeneous LLZ electrolyte was prepared using PCM and HIP. A Li-ion battery was fabricated using the LLZ electrolyte and a gelled $LiFePO_4$ (LFP) composite cathode by adding a conductive IL.

2. Experimental

LLZ samples were synthesized according to a reported method [37]. Anhydrous $LiNO_3$ (0.0714 mol), $La(NO_3)_3{\cdot}6H_2O$ (0.03 mol), $ZrO(NO_3)_2{\cdot}8H_2O$ (0.02 mol), and $Al(NO_3)_3{\cdot}9H_2O$ (0.0022 mol) were dissolved in ultrapure water. The excesses of Li and Al were 2% and 1.35 wt%, respectively. Citric acid (0.36 mol) and ethylene glycol (1.44 mol) were added to the nitrate solution as complexing agents. The mixture was heated at 130 °C to promote polymerization and remove excess solvents. By heating at 130 °C, the mixture became more viscous and turned into the brown resin. The resin was further heated at 450 °C to promote carbonization and turned into black solid mass. This black mass precursor was calcined at 700 °C for 5 h. After the calcination, the powder was pressed into a pellet, and the pellet was sintered at 1180 °C under an O_2 atmosphere. The sintered LLZ pellets were HIP-treated at 1180 °C and 132 MPa for 2 h. The concentrations of Li, La, Zr, and Al in LLZ were measured by inductively coupled plasma atomic emission spectroscopy (SPS3100; SII NanoTechnology Inc., China). Scanning transmission electron microscopy (STEM) was performed at 200 kV and a beam current of 20 mA (JEM-RM200F JEOL).

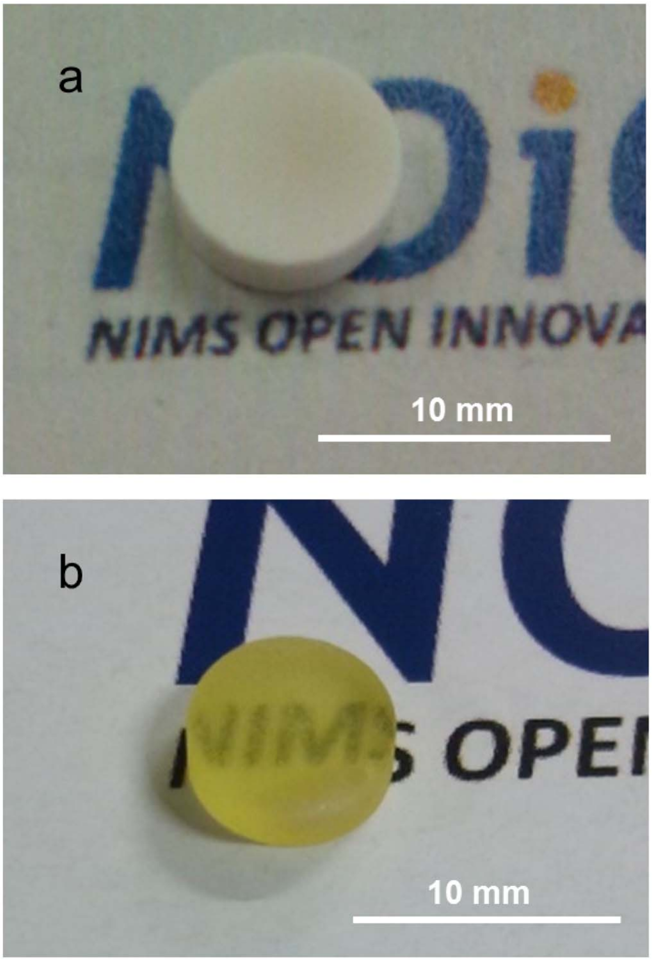

Fig. 1. Photographic images of the LLZ samples (a) before and (b) after HIP treatment.

The conductivities of the prepared samples were measured using an impedance analyzer (Solartron 1260) from 0.1 Hz to 1 MHz with a voltage amplitude of 10 mV. Au was sputtered onto both sides of the pellet to ensure electrical contact. To fabricate the battery cell, a composite cathode was prepared by mixing LFP with KB, and then IL was added [48]. IL was prepared from 1 M lithium bis(trifluoromethanesulfonyl)imide dissolved in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. Symmetrical cells were fabricated by pressing composite cathode electrodes from both sides of the LLZ pellet. The thickness of LLZ sample was 1 mm and the electrode area was 0.20 cm^2. A Li-ion battery with a composite cathode (LFP-c)/LLZ/Li configuration was fabricated by putting LFP-c and Li metal on each surface of LLZ. The electrode area was 0.20 cm^2. The electrochemical properties of the LFP-c/LLZ/Li cell were investigated by cyclic voltammetry and galvanostatic measurements.

3. Results and discussion

The LLZ sample was prepared by PCM synthesis [36], and HIP treatment further densified the synthesized LLZ sample. Fig. 1a and b shows images of the prepared LLZ samples before and after the HIP treatment, respectively. The LLZ pellet became transparent after the treatment. This transparency indicates that the LLZ sample was dense and consisted of a single phase with few impurity particles or pores. Table 1 shows the composition ratio of Li, La, Zr, and Al in LLZ measured by ICP-AES. The composition ratio of LLZ was almost same as charge ratio of the raw materials. Fig. 2 shows the XRD pattern of the