Solid State Ionics 326 (2018) 52–57

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Fabrication and charge-discharge reaction of all solid-state lithium battery using $Li_{4-2x}Ge_{1-x}S_xO_4$ electrolyte

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ARTICLE INFO

Keywords:
All solid-state battery
Oxide electrolyte
LISICON
Lithium batteries

ABSTRACT

Bulk-type solid-state batteries using a LIthium Super Ionic CONductor (LISICON)-based oxide electrolyte, $Li_{4-2x}Ge_{1-x}S_xO_4$, were assembled by spark plasma sintering (SPS) and electric furnace sintering (FS), and their charge-discharge performances were investigated. $Li_{4-2x}Ge_{1-x}S_xO_4$, which has a γ-Li_3PO_4-type structure, was synthesized by conventional solid-state reaction. The total ionic conductivity of the $Li_{3.6}Ge_{0.8}S_{0.2}O_4$ sample sintered at 600 °C by SPS was 2×10^{-5} S cm^{-1} at room temperature, which is comparable to the bulk conductivity of the material sintered at 800–1100 °C by FS. No impurity peaks were observed in the X-ray diffraction patterns of the $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$-$Li_{3.6}Ge_{0.8}S_{0.2}O_4$ mixture even after high-temperature sintering at 900 °C by FS. The solid-state cells of laminated $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ cathode and $Li_{3.6}Ge_{0.8}S_{0.2}O_4$ electrolyte co-sintered by SPS at 600 °C and FS at 900 °C exhibited first discharge capacities of 130 and 92 mAh g^{-1}, respectively, at 60 °C. These experimental results confirm that the LISICON-based material, $Li_{4-2x}Ge_{1-x}S_xO_4$, exhibits thermal compatibility to the active material and relatively high lithium ion conductivity, which lead to the high charge-discharge performance of the bulk-type all-solid-state cell.

1. Introduction

All-solid-state lithium batteries with a non-flammable solid electrolyte have recently attracted significant attention owing to their high power and energy density and improved safety compared with the current battery system that uses a highly reactive organic electrolyte [1–3]. An electrode-electrolyte composite electrode usually shows large contact resistance for ion transfer at the interface. Sulfide electrolytes are extensively studied because their high ionic conductivity and suitable formability for the construction of the interface enable the cell to achieve a high charge-discharge performance [1,2,4,5]. On the other hand, because oxide electrolytes have lower moisture sensitivity and toxicity than sulfide electrolytes, they are anticipated to improve the reliability of the battery. However, it is a challenge to use these electrolytes to construct a well-formed electrode-electrolyte composite electrode mainly owing to their poor deformability at room temperature. Although a sintering process is necessary to create good contact between the electrode and electrolyte, high-temperature sintering often leads to the formation of resistive interfacial phases [6–8]. Either low-temperature sintering or the use of an oxide electrolyte with high thermal stability against the electrode during the sintering process is an important factor in providing a reversible charge-discharge reaction during battery operation. Spark plasma sintering (SPS) is a well-known technique that enables low-temperature or rapid sintering, and it is used to produce dense ceramics [7,9,10]. Although this technique has been applied to achieve good contact between the electrode and solid electrolyte within a short period, using it for the co-sintering of a $LiTi_2(PO_4)_3$ and $LiCoO_2$ mixture resulted in the formation of interfacial impurity [7]. Recently, we have reported that a well-defined interface between $LiCoO_2$ and the Li_2CO_3-Li_3BO_3 electrolyte was achieved without formation of any impurity phases by co-sintering the materials by SPS. This resulted in the reversible lithium (de-)intercalation reactions of the $LiCoO_2$ cathode material for the bulk-type solid-state cell [10]. The Li_2CO_3-Li_3BO_3 electrolyte has high thermal stability against the electrode material at the co-sintering temperature; however, it exhibits low conductivity at 30 °C (6.5×10^{-7} S cm^{-1}) [11], which could limit the reversible capacity of the cell. An oxide electrolyte with high ionic conductivity is therefore desirable to further improve the battery performance of an all-solid-state cell.

LIthium Super Ionic CONductor (LISICON)-related materials with a γ-Li_3PO_4 type structure in the germanium system have conductivities of approximately 10^{-5} S cm^{-1} at room temperature and form a solid solution with many elements for a wide range of composition [12–16]. In particular, $Li_4(Ge, Ti)O_4$-$Li_3(As, V)O_4$ and Li_4GeO_4-Li_2SO_4 have conductivities of 2–4×10^{-5} S cm^{-1} at room temperature [12,16]. In a preliminary experiment, LISICON materials exhibited high thermal

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https://doi.org/10.1016/j.ssi.2018.09.011
Received 30 June 2018; Received in revised form 17 September 2018; Accepted 17 September 2018
0167-2738/

stability against layered rock salt electrodes, in contrast to well-known oxide electrolytes with high ionic conductivity, such as NASICON and garnet-type structure [7,8]. Thus, these materials can potentially be used as electrolytes for a bulk-type all-solid-state battery to improve its limited battery performance. In this study, we focused on the LISICON-based material, Li_4GeO_4-Li_2SO_4 ($Li_{4\text{-}2x}Ge_{1\text{-}x}S_xO_4$), which exhibits high ionic conductivity and consists of typical metal cations acting as the solid electrolyte. Its thermal compatibility to the layered rock salt cathode, $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$, during the electric furnace sintering (FS) and SPS processes was examined. Using $Li_{3.6}Ge_{0.8}S_{0.2}O_4$ as the electrolyte, the charge-discharge characteristics of all-solid-state cells assembled by these sintering processes were investigated.

2. Experimental

During the synthesis of the electrolyte materials, oxygen flow was maintained to prevent Li_2CO_3 formation on the prepared powder as much as possible [17]. Li_4GeO_4 was prepared using the starting materials, $LiOH{\cdot}H_2O$ (99.0% purity, Kojundo Chemical Laboratory, Japan) and GeO_2 (99.0% purity, Kojundo Chemical Laboratory, Japan). Appropriate amounts of the compounds were weighed to obtain a molar ratio of 4:1, and then the mixture was ground in an agate mortar. The powder mixture was fired at 600 °C for 12 h and subsequently pelletized and sintered at 700 °C for 12 h. $Li_{4\text{-}2x}Ge_{1\text{-}x}S_xO_4$ (x = 0.1–0.4) was synthesized by sintering the powder mixture of Li_4GeO_4 and Li_2SO_4. Appropriate amounts of ground Li_4GeO_4 and Li_2SO_4 (99.0% purity, Kojundo Chemical Laboratory, Japan) were weighed to obtain the desired molar ratio, and then the compounds were mixed in an agate mortar within an Ar-filled glove box. The final mixture was pressed into pellets and heated at 900 °C for 12 h. Phase identification of the $Li_{4\text{-}2x}Ge_{1\text{-}x}S_xO_4$ samples was carried out by powder X-ray diffraction (XRD) using an X-ray diffractometer with Cu Kα radiation (Miniflex600, Rigaku, Japan). Lattice parameters were refined using the Rietveld refinement program, RIETAN-FP [18]. The $Li_{4\text{-}2x}Ge_{1\text{-}x}S_xO_4$ samples were crushed in a ZrO_2 pot with five 5-mm ZrO_2 disks using vibration milling (MC-4A, Ito Seisakusho, Japan). The crushed samples were sandwiched between the Li-ion-blocking gold electrodes that will be used in the AC impedance measurement, and then placed in a 10-mm carbon die. To prepare the samples by SPS, the die was heated to 600 °C at a rate of $\approx 50\,°C\,min^{-1}$ with a DC sawtooth-pulsed electric current under a pressure of 30 MPa (pulse length: 2.5 ms, number of consecutive pulses: 14 times, interval after consecutive pulses: 5 ms) in the SPS instrument (SPS-515S, Sumitomo Coal Mining, Japan). The After reaching the desired temperature, the conditions were kept for 1 min, after which the applied current was stopped, pressure was released, and the sample was cooled to room temperature. The ionic conductivity of the sintered samples was measured by the AC impedance method under Ar atmosphere at room temperature. An alternating voltage with an amplitude of 50 mV was applied in the frequency range between 1 and 30 MHz using the 1260 Frequency Response Analyzer (Solartron Analytical, UK).

The compatibility between the cathode and electrolyte materials sintered by FS and SPS was examined by XRD. $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (average particle size = 10.0 μm, Nippon Chemical Industrial, Japan) and $Li_{3.6}Ge_{0.8}S_{0.2}O_4$ were mixed (1:1 w/w%) in an agate mortar. The mixture was pressed under a pressure of 800 MPa in a 10-mm stainless steel die to make a pellet, which was then sintered at 900 °C for 2 h with oxygen flowing through the electric furnace. To prepare the samples by SPS, the mixture was sandwiched between the titanium electrodes, placed in a 10-mm carbon die, and sintered at 600 °C under a pressure 30 MPa for 1 min in Ar atmosphere.

A composite electrode powder consisting of 60 wt% $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ and 40 wt% $Li_{3.6}Ge_{0.8}S_{0.2}O_4$ (i.e., $Li_{4\text{-}2x}Ge_{1\text{-}x}S_xO_4$, x = 0.2) electrolyte was prepared by mixing the materials in an agate mortar. A disk-shaped half-cell pellet containing the composite electrode/electrolyte layer was prepared by SPS and FS for the charge-discharge measurement. The $Li_{3.6}Ge_{0.8}S_{0.2}O_4$ electrolyte powder (30 mg) was placed in a 10-mm stainless steel die, on top of which was placed 10 mg of the composite electrode powder. The powders were pressed together under a pressure of 800 MPa, and then sintered at 800–900 °C for 2 h with oxygen flowing through the electric furnace. After sintering, a gold current collector was deposited onto the composite electrode by DC sputtering. The same amounts of the composite electrode and electrolyte powders were used for SPS. The composite electrode powder and gold current collector were placed onto the $Li_{3.6}Ge_{0.8}S_{0.2}O_4$ electrolyte powder in a 10-mm carbon die, which was then heated at 600 °C for 1 min under a pressure of 30 MPa in Ar atmosphere in the SPS instrument. Lithium foil was used as a counter electrode. A polyethylene oxide (PEO)-based polymer electrolyte film (LiTFSA/EO = 0.06, Osaka Soda, Japan) was placed between the lithium foil and electrolyte side of the composite electrode/electrolyte pellet to reduce the interfacial resistance upon adhesion [10]. The chargedischarge characteristics of the all-solid-state cells assembled by FS and SPS were examined in the range of 2.0–4.2 V with a constant current of $32\,\mu A\,cm^{-2}$ ($4.2\,mA\,g^{-1}$ of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$) at 60 °C using a charge-discharge testing apparatus (BST2004, Nagano, Japan). The cross-sectional microstructures of the composite electrode/electrolyte sintered by SPS and FS were observed using scanning electron microscopy (SEM, JSM-6510LA, JEOL Ltd., Japan). The cross-sections of the samples were prepared by polishing using Ar ion-milling (IB-09020CP, JEOL Ltd., Japan).

3. Results and discussion

Fig. 1a shows the powder XRD patterns of $Li_{4\text{-}2x}Ge_{1\text{-}x}S_xO_4$ samples with a composition within the range of $0 \leq x \leq 0.4$. The sample with $x = 0$ exhibits the diffraction peaks attributable to the Li_4GeO_4 phase having the *Cmcm* space group [12]. On the other hand, the samples with $x \neq 0$ had diffraction patterns that mainly correspond to the LISICON phase having a γ-Li_3PO_4-type structure (space group *Pnma*) [12]. The peaks derived from the secondary phase are not observed in samples with x = 0.1–0.3. These results confirm the formation of the LISICON phase upon substitution of Ge by S in Li_4GeO_4. The peaks gradually shift to higher angle with increasing x, indicating the formation of solid solution. The sample with $x = 0.4$ shows a two-phase character due to the LISICON phase and β-Li_2SO_4. The lattice parameters of $Li_{4\text{-}2x}Ge_{1\text{-}x}S_xO_4$ (x = 0.1–0.4), refined using the RIETAN-FP program, are shown in Fig. 1b. The a and c axes linearly decrease, while b slightly increases, with increasing x. The cell volume decreases linearly with increasing x because of the replacement of Ge^{4+} (r = 0.39 Å) by the smaller S^{6+} cation (r = 0.12 Å) in the structure [12,19].

The composition dependence of the ionic conductivity at room temperature was determined for the $Li_{4\text{-}2x}Ge_{1\text{-}x}S_xO_4$ (x = 0.1–0.4) samples sintered at 600 °C by SPS, and the Nyquist plots are shown in Fig. 2a. The spectra contain a semicircle and spike in the high- and low-frequency regions, respectively. The semicircle likely corresponds to the bulk resistance of $Li_{4\text{-}2x}Ge_{1\text{-}x}S_xO_4$, while the spike is due to charge polarization at the blocking electrode. Note that although grain-boundary resistance is often observed for oxide electrolyte pellets sintered by FS, this resistance is minimized after SPS [17]. The resistance was determined from the intercept of the spike with the real axis. The ionic conductivities of the $Li_{4\text{-}2x}Ge_{1\text{-}x}S_xO_4$ (x = 0.1–0.4) samples, calculated from the bulk resistance, are summarized in Fig. 2b. The conductivity increases from x = 0.1 to 0.2, but decreases from x = 0.2 to 0.4 because of an optimization in the carrier concentration and cooperative interactions between the mobile lithium ions [12]. In this study, the highest conductivity, $2 \times 10^{-5}\,S\,cm^{-1}$, was obtained for $Li_{3.6}Ge_{0.8}S_{0.2}O_4$, which is comparable to the bulk conductivity of the material sintered at 800–1100 °C by FS [12]. These results demonstrate that $Li_{4\text{-}2x}Ge_{1\text{-}x}S_xO_4$ was successfully sintered by SPS at a lower temperature than that used in FS, and the grain-boundary resistance was reduced by SPS. Therefore, $Li_{3.6}Ge_{0.8}S_{0.2}O_4$ was used as the separator layer and electrolyte material in the composite electrode of the solid-state cell fabricated in this study.