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Raman imaging for $LiCoO_2$ composite positive electrodes in all-solid-state lithium batteries using $Li_2S-P_2S_5$ solid electrolytes

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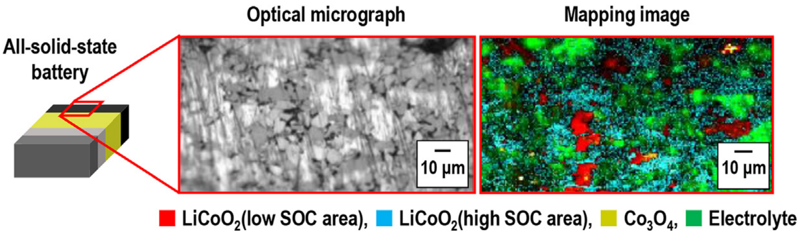
HIGHLIGHTS

- Raman microscopy is conducted for composite electrodes in all-solid-state cells.
- Raman spectral changes of the electrodes are observed during charge test.
- Local state-of-charge distribution map is obtained by Raman mapping.
- Raman mapping image indicates distributions of reactions exist in the electrode.

GRAPHICAL ABSTRACT



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ABSTRACT

A composite positive electrode in an all-solid-state battery is prepared by mixing $LiCoO_2$ particles and $Li_2S-P_2S_5$ solid electrolytes. Raman spectroscopy is conducted for the composite positive electrodes before and after the initial charging process. Raman spectral changes are observed, which corresponds to structural changes of $LiCoO_2$ particles during the charge test. However, some spectra indicate that several $LiCoO_2$ particles show no structural changes although the cell is fully charged. A local state-of-charge (SOC) distribution map of the composite electrode is obtained by Raman mapping. The mapping image after the charge test shows that distributions of reactions exist in the composite positive electrode.

1. Introduction

Lithium ion batteries (LIBs) have been used as power sources for portable electronics devices because of their high energy density, light weight and long cycle life [1]. Recently, large-scale LIBs have attracted much attention as power sources for electric vehicles and stationary energy storage systems. However, conventional LIBs have risks of leakage and explosion of organic liquid electrolytes. It is important to solve such safety issues with increasing battery size [2]. All-solid-state batteries with nonflammable inorganic solid electrolytes, an alternative to conventional inflammable organic liquid electrolytes, are next generation batteries with low risk of leakage and explosion. All-solid-state batteries are categorized into bulk-type batteries and film-type batteries. Bulk-type batteries, which use composite electrodes of active materials and solid electrolytes, are especially capable of having high energy density. We have investigated the electrochemical performance of bulk-type all-solid-state cells using a $LiCoO_2$ composite positive electrode and a $Li_2S-P_2S_5$ solid electrolyte [3–5]. Rechargeable all-solid-state cells can be fabricated by pressing positive and

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negative electrode layers and a solid electrolyte layer at room temperature [6]. One of these cells, which showed good cell performance, was charged and discharged during 700 cycles at 25 °C [3]. To improve the cell performance, electrochemical reactions at electrode-electrolyte interfaces should be studied.

There are several reports investigating physical and electrochemical properties of positive electrode active materials in the cells using liquid electrolytes during charge–discharge cycling by using various analytical methods such as X-ray diffraction [7], X-ray absorption spectroscopy [8,9], scanning transmission X-ray microscopy [10], nuclear magnetic resonance (NMR) [11] and atomic force microscope (AFM) [12]. Raman spectroscopy is also suitable for investigating electrochemical reaction of active materials because Raman spectral changes of a composite electrode are closely related to the structural changes of active materials during charge–discharge cycling. There are several reports regarding Raman spectral changes of $LiCoO_2$ composite electrodes in lithium cells using liquid electrolytes during the charging process [13,14]. Furthermore, Raman mapping was conducted because of its feature of high spatial resolution and surface sensitivity [15–17]. Mapping images enable us to evaluate state-of-charge (SOC) distributions of each active material in electrodes. However, there are no reports conducting Raman spectroscopy for $LiCoO_2$ composite electrode in all-solid-state lithium cells.

$LiCoO_2$ composite electrodes in all-solid-state batteries have many solid–solid interfaces, and thus electrochemical reactions at the interfaces are complicated. Furthermore, investigations of SOC distributions in the electrodes have not been carried out. Clarification of these issues is important to improve electrochemical performances of all-solid-state cells. In this study, *Ex-situ* Raman spectroscopy was carried out for cross-section of $LiCoO_2$ composite positive electrodes in bulk-type all-solid-state lithium batteries to observe spectral changes during the charging process. Moreover, Raman mapping was conducted for $LiCoO_2$ composite positive electrodes to investigate local SOC distributions.

2. Experimental

2.1. Preparation of solid electrolyte

The $75Li_2S\cdot25P_2S_5$ (mol%) glass used as a solid electrolyte was prepared using a mechanical milling technique. Li_2S (Idemitsu Kosan, 99.9%) and P_2S_5 (Aldrich, 99%) crystalline powders were used as starting materials for sample preparation. The batches (1 g) of these mixed materials with the composition of $75Li_2S\cdot25P_2S_5$ (mol%) were mechanically milled at 510 rpm for 45 h using a planetary ball mill (Pulverisette 7; Fritsch) with a zirconia pot (45 mL volume) and 500 zirconia balls (4 mm diameter).

2.2. Fabrication of all-solid-state cells

$LiNbO_3$-coated $LiCoO_2$ was used as a positive electrode active material because a $LiNbO_3$ buffer layer decreases the interfacial resistance between $LiCoO_2$ particles and solid electrolytes [18]. $LiNbO_3$-coated $LiCoO_2$ particles (Toda Kogyo Co., 10 μm) and the $75Li_2S\cdot25P_2S_5$ (mol%) glass particles (2–5 μm [6]) with a weight ratio of 80 : 20 were mixed using an agate mortar to prepare composite positive electrodes. The optimized weight ratio to operate the cells was 70: 30 [5], and the ratio studied here includes larger amounts of $LiCoO_2$, that may lead to a partial formation of insufficient Li^+ ion conduction paths to $LiCoO_2$. Moreover, the amount of $LiCoO_2$ particles in the composite electrode with the ratio of 80 : 20 is larger and more $LiCoO_2$ particles are able to be examined by Raman microscopy. The ratio of 80 : 20 was thus selected in this study. Indium foil (99.999%; Furuuchi Chemical Corp.) was used as a negative electrode. A bilayer pellet consisting of the composite positive electrode (10 mg) and the $75Li_2S\cdot25P_2S_5$ (mol%) glass (80 mg) was obtained by pressing under 360 MPa. Indium foil was then attached to the bilayer pellet and pressed with stainless steel powder (SUS304L, Kojundo Chemical) (150 mg) used as a current collector under 240 MPa. A cuboid pellet ($8\ mm \times 4\ mm \times 2\ mm^t$) pressed using two stainless-steel plates which were used as current collectors for both positive and negative electrodes. Fig. 1(A) and (B) show a schematic diagram of the four-layered pellet and a photograph of the all-solid-state cell used in this study. The white box in Fig. 1(B) denotes the pellet. All the processes for preparation of solid electrolyte and fabrication of all-solid-state cells were carried out at room temperature in a dry Ar-filled glove box.

2.3. Electrochemical measurements

The cells were charged to 4.2 V (Li^+/Li) or different capacities of 20, 40, 60 and 80 mAh per gram of $LiCoO_2$ using a charge–discharge measuring device (BTS-2004; Nagano Co Ltd., Japan). The measurements were conducted at 25 °C under a current density of $0.064\ mA\ cm^{-2}$.

2.4. Raman spectroscopy

After the 1st charging process, the layered pellet of In/$75Li_2S\cdot25P_2S_5$ (mol%)/$LiCoO_2$ was dismounted from the all-solid-state cells. The cells were sealed in a container with an optical flat glass window under dry Ar atmosphere. *Ex-situ* Raman spectroscopy was carried out for cross-section of the positive electrodes by Raman microscopy (LabRAM HR-800; Horiba-Jobin Yvon) with a green laser (532 nm) and a 50× objective (NA = 0.35, Olympus). The laser power at the sample was *ca.* 1 mW with a laser spot size of *ca.* 2 μm. Acquisition time for each spectrum was 360 s. At least 10 spectra were collected at the different locations on the positive electrode.

Raman imaging was done for a surface part of the positive electrodes before and after the 1st charging process using a Raman microscope (RAMANtouch; Nanophoton). An Ar ion-milling technique was done for removing irregularities on the surface using an ion-milling system (IM4000; HITACHI). The laser beam was focused onto the sample using a 50× objective (NA = 0.70, Nikon) with excitation at 532 nm. The intensity of the laser beam was *ca.* $5.3 \times 10^4\ W\ cm^{-2}$. Before conducting Raman spectroscopy, the morphologies of the electrodes prepared by Ar ion-milling technique were investigated by using scanning electron microscopy (SEM) (SU8220; HITACHI).

3. Results and discussion

All-solid-state cells (In/Li_2S–P_2S_5 glass/$LiCoO_2$) were charged to 4.2 V (vs. Li^+/Li) or different capacities of 20, 40, 60 and 80 $mAh\ g^{-1}$. After the charge test, Raman spectroscopy was conducted for cross-section of the $LiCoO_2$ composite positive electrode layers. Fig. 2 shows the schematic diagram of the cross-section of the all-solid-state cell and the optical micrograph of the cross-section of the positive electrode selected by a red box in the diagram. The laser beam was focused on $LiCoO_2$ particles (bright ones) with a laser spot size of *ca.* 2 μm. At least 10 particles were measured for each positive electrode of the cells charged to the different capacities.

Fig. 3(A) shows the initial charge curve of the all-solid-state cell. Fig. 3(B) shows the Raman spectra of $LiCoO_2$ electrode layers at the different charge capacities. The labels in Fig. 3(A) and (B) are as follows: (a) 0, (b) 20, (c) 40, (d) 60, (e) 80 and (f) 103 $mAh\ g^{-1}$. A typical spectrum at each capacity is shown in Fig. 3(B). There are