



Optical microscopic observation of graphite composite negative electrodes in all-solid-state lithium batteries



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ABSTRACT

Composite graphite negative electrodes were prepared by mixing graphite particles and $75\text{Li}_2\text{S}\cdot 25\text{P}_2\text{S}_5$ (mol%) glass particles with weight ratios of $x:100 - x$ ($x = 50, 60$ and 70). The cell with the $x = 50$ electrode showed the highest reversible capacity of more than 250 mAh g^{-1} . Optical microscopy was conducted for each composite electrode after electrochemical lithiation to investigate reaction distributions by color changes of graphite particles. In the $x = 50$ electrodes, almost all the graphite particles changed to gold color, suggesting that the graphite particles were fully lithiated. *In situ* optical microscopy was also carried out for the composite graphite electrode to monitor color changes of graphite particles directly during charge-discharge tests.

1. Introduction

In recent years, there has been an increasing interest in all-solid-state batteries with high safety due to the use of non-flammable inorganic solid electrolyte instead of flammable organic liquid electrolyte [1]. To apply large-scale batteries to power sources of electric vehicles, high energy density and high cycle performance are absolutely necessary [2].

Bulk-type all-solid-state batteries employ composite electrodes containing active electrode materials and solid electrolytes. Solid electrolyte particles play an important role in conveying ions to active materials in composite electrode layers. Although high energy density of the batteries will be achieved by increasing amounts of active materials in the composite electrodes, decreasing the amounts of solid electrolytes in the electrodes tends to cause insufficient contacts between solid electrolyte particles and active material particles. In our previous report, Raman mapping techniques revealed that electrochemical reactions did not proceed uniformly at insufficient contacts between LiCoO_2 and solid electrolyte particles [3,4].

Graphite is widely used as a negative electrode material for commercial lithium ion batteries with the advantages of low voltage and high cycle performance [5,6]. However, few researchers have examined graphite composite electrodes in all-solid-state lithium batteries [7–11]. Takada et al. discovered that graphite showed reversible electrochemical reactions when using $44\text{LiI}\cdot 38\text{Li}_2\text{S}\cdot 18\text{P}_2\text{S}_5$ (mol%) glass solid electrolyte [7]. Takada and Seino et al. constructed all-solid-state lithium batteries (Graphite/ $44\text{LiI}\cdot 38\text{Li}_2\text{S}\cdot 18\text{P}_2\text{S}_5$ glass/ LiCoO_2), which operated under the current densities of $7.2 \mu\text{A cm}^{-2}$ – 1.4 mA cm^{-2} at

25°C [8,9]. Takeuchi et al. applied graphite-solid electrolyte composite negative electrodes to all-solid-state lithium batteries with Li_2S positive electrodes [10,11]. Seino et al. fabricated a half-cell (Graphite/ $70\text{Li}_2\text{S}\cdot 30\text{P}_2\text{S}_5$ (mol%) glass ceramic/Lithium-Indium alloy) and the cell showed a reversible capacity of 251 mAh g^{-1} when cycled between -0.62 and 1.5 V at room temperature under the current density of $10 \mu\text{A}$ ($12.7 \mu\text{A cm}^{-2}$) [9]. The graphite mixed with the solid electrolyte with the weight ratio of 50: 50, and only this composition was examined in the paper [9]. To achieve higher energy density in all-solid-state cells, it is important to investigate charge-discharge properties and reaction distributions of the electrodes with large amounts of graphite in the composite electrode.

Graphite changes its stage structures during a lithiation process. Inaba et al. and Dahn respectively investigated the stage structures by *in situ* Raman spectroscopy [12] and *in situ* X-ray diffraction measurements [13]. Three plateaus were observed in the potential profile at ca. 200, 100 and 70 mV. The first, second and third plateaus corresponded to transitions from dilute stage 1 to stage 4, from stage 2L (liquid-like stage 2 phase) to stage 2, and from stage 2 to stage 1, respectively. Graphite changes its colors from black via blue and red to gold during lithiation [14,15]. The color changes enable us to evaluate reaction distributions in graphite electrodes. In this paper, optical microscopy was conducted for lithiated graphite composite electrodes with various compositions of solid electrolyte and graphite to investigate reaction distributions in the composite electrodes by color changes of graphite particles.

In situ measurement is a suitable technique to examine electrochemical reaction mechanisms in detail [16,17]. To monitor electrodes

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directly during charge-discharge process for *in situ* measurements, specially designed cells and measurement setups are needed [17]. In previous reports of graphite electrodes in lithium ion batteries using a liquid electrolyte, reaction distributions and a Li plating mechanism were clarified by *in situ* optical microscopy during charge-discharge tests [14,15]. However, no research on *in situ* optical microscopy for graphite composite negative electrodes has been done in all-solid-state lithium batteries. In this study, a hand-made cell for *in situ* measurements was designed to monitor color changes of graphite particles directly during charge-discharge tests.

The purpose of the present study is to examine suitable compositions to achieve a uniform electrode-reaction by investigating reaction distributions in graphite composite negative electrodes using optical microscopy. Moreover, *in situ* optical microscopy was carried out for graphite negative electrodes for the first time.

2. Experimental

The $75\text{Li}_2\text{S}\cdot 25\text{P}_2\text{S}_5$ (mol%) glass solid electrolyte was prepared by a mechanical milling technique. Li_2S (Mitsuba Chemicals Co., Ltd., 99.9%) and P_2S_5 (Aldrich, 99%) crystalline powders were mixed in an agate mortar. The batches (1 g) of these mixed materials with a stoichiometric ratio were mechanically milled at the rotation speed of 510 rpm for 45 h using a planetary ball mill apparatus (Pulverisette 7; Fritsch) with a zirconia pot (45 mL volume) and 500 zirconia balls (diameter in 4 mm). The diameter of the $75\text{Li}_2\text{S}\cdot 25\text{P}_2\text{S}_5$ glass particle was about 15 μm .

Smaller-sized $75\text{Li}_2\text{S}\cdot 25\text{P}_2\text{S}_5$ glass solid electrolyte (diameter in ca. 3 μm) was prepared by a wet mechanical milling technique with heptane and dibutyl ether [4,18]. Smaller-sized solid electrolyte was used in composite electrodes to increase contact points between graphite and solid electrolyte.

Composite negative graphite electrodes were prepared by hand-mixing graphite particles (CGB-10, Nippon Graphite Industries, Ltd.) (diameter in ca. 10 μm) and $75\text{Li}_2\text{S}\cdot 25\text{P}_2\text{S}_5$ glass particles with weight ratios of $x:100-x$ ($x = 50, 60$ and 70) corresponding to the volume ratios of 45:55, 55:45 and 66:34, respectively. The $75\text{Li}_2\text{S}\cdot 25\text{P}_2\text{S}_5$ glass particles (diameter in ca. 15 μm) (80 mg) were pressed to obtain a solid electrolyte layer. The graphite composite negative electrode (10 mg) was grounded on the solid electrolyte layer and then pressed at 360 MPa. A lithium foil (99.9%, 0.25 mm^2 ; Furuuchi Chemical Corp.) ($\phi = 8$ mm) and an indium foil (99.999%, 0.3 mm^2 ; Furuuchi Chemical Corp.) ($\phi = 9$ mm) were attached to the bilayer pellet as a counter electrode and pressed at 120 MPa. The pellets were sandwiched with two stainless steel disks as current collectors. All the processes were conducted in an Ar-filled glove box at room temperature. The cells were charged (lithiated) and discharged (delithiated) under a current density of 0.13 mA cm^{-2} at 25 °C with a cut-off voltage between -0.62 and 1 V (vs. Li-In) using a charge-discharge measuring device (BTS-2004; Nagano Co Ltd., Japan).

After the 11th charge test, the cells were disassembled. Optical microscopy and Raman spectroscopy were conducted for surface (current collector side) and cross-section of each graphite composite negative electrode using a Raman microscope (LabRam HR-800; Horiba-Jobin Yvon) with a green laser (532 nm) and a 50 \times objective lens (NA = 0.50, Olympus). Before and after the charge-discharge test, morphologies of the graphite negative electrode layers prepared by Ar ion-milling technique (IM4000; HITACHI) were examined by using a scanning electron microscope (SEM) (SU8220; HITACHI).

An electrochemical cell was fabricated for an *in situ* measurement as follows. Fig. 1 (a) shows a schematic diagram of the *in situ* cell. It has five layers consisting of stainless steel powder, graphite electrode, $75\text{Li}_2\text{S}\cdot 25\text{P}_2\text{S}_5$ glass, lithium-indium alloy and stainless steel foil. Stainless steel powder (SUS304L, Kojundo Chemical) (150 mg) was pelletized in 10 mm ϕ by pressing at 180 MPa and then was punched to make a hole ($\phi \cong 1$ mm) at the center of the pellet. Graphite and solid

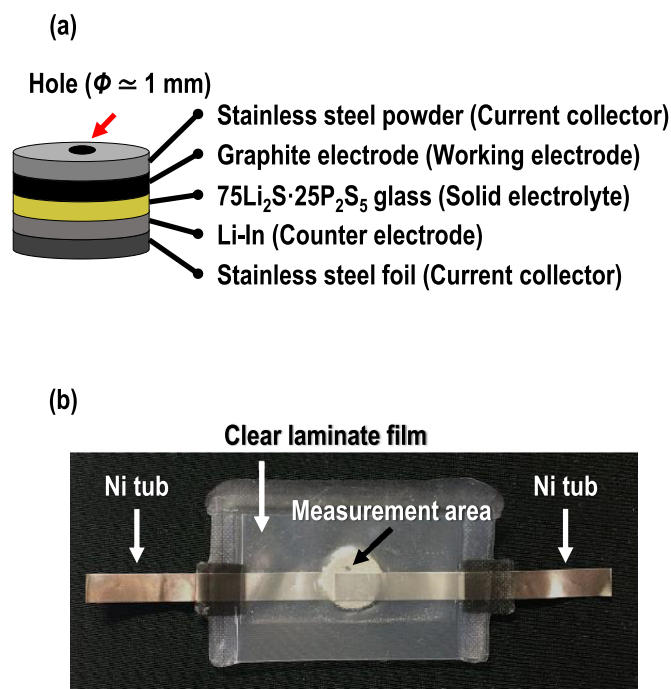


Fig. 1. (a) Schematic diagram of a five-layered pellet. Graphite electrode was monitored through the hole in the stainless steel powder pellet. (b) Photograph of an all-solid-state cell used for *in situ* optical microscopy.

electrolyte were mixed with the weight ratio of 50:50 to obtain a composite electrode. A bilayer pellet of the graphite composite electrode layer and the solid electrolyte layer was prepared by pressing slightly. The stainless steel pellet mentioned above was put on the bilayer pellet and pressed at 360 MPa for 5 min. An indium foil ($\phi = 8$ mm), a lithium foil ($\phi = 7$ mm) and a stainless steel foil (SUS316L; Nilaco Corp.) ($\phi = 9.9$ mm) were attached to the pellet and then pressed at 50 MPa. The pellet was sealed into a clear laminate film with Ni tubes under vacuum as shown in Fig. 1 (b). *In situ* optical microscopy was carried out for the graphite electrode through the hole on the stainless steel pellet by using a digital microscope (3R-WM401WIFI; 3R Systems Corp.). A charge-discharge test was conducted under a current density of 0.064 mA cm^{-2} at room temperature using a charge-discharge measuring apparatus (580-NOHFR; Scribner Associated INC.). The cell was charged to 300 mAh g^{-1} and discharged to 1 V (vs. Li-In) at the initial cycle and then charged to 200 mAh g^{-1} . Optical micrographs were obtained every 10 mAh g^{-1} . After the charging process to 200 mAh g^{-1} , the cell was disassembled and SEM observation was conducted for the cross-section of the electrode prepared by Ar ion-milling technique.

3. Results and discussion

Fig. 2 (a) shows the initial charge-discharge curves of the cells using the composite graphite electrodes containing graphite and $75\text{Li}_2\text{S}\cdot 25\text{P}_2\text{S}_5$ glass with the weight ratios of $x:100-x$ ($x = 50, 60$ and 70). The initial reversible capacities of the cells using $x = 50, 60$ and 70 electrodes were 270, 266 and 100 mAh g^{-1} , respectively. Fig. 2 (b) shows cycle performances of the cells. All the cells did not exhibit a noticeable capacity loss after the 2nd cycles. The cell with the $x = 70$ electrode showed extremely lower capacities than the cells with the $x = 50$ and 60 electrodes.

Fig. 3 shows cross-sectional SEM images of each electrode before the charge-discharge test. Light and dark contrasts denote solid electrolyte (SE) and graphite, respectively. As shown in Fig. 3 (c), contact areas between graphite and solid electrolyte decreased in the $x = 70$

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