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Sulfur–carbon composite electrode for all-solid-state Li/S battery with Li_2S–P_2S_5 solid electrolyte

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ABSTRACT

All-solid-state Li/S batteries with Li_2S–P_2S_5 glass–ceramic electrolytes were fabricated and their electrochemical performance was examined. Sulfur–carbon composite electrodes were prepared by grinding with a mortar and milling with a planetary ball-mill apparatus. Milling of a mixture of sulfur, acetylene black and the Li_2S–P_2S_5 glass–ceramic electrolyte resulted in the amorphization of sulfur and a reduction in the particle size of the mixture. The charge–discharge properties of all-solid-state cells with the composite electrode were investigated at temperatures from −20 °C to 80 °C. The cells retained a reversible capacity higher than 850 mAh g^{-1} for 200 cycles under 1.3 mA cm^{-2} (333 mA g^{-1}) at 25 °C. The cell performance was influenced by the crystallinity of sulfur and the particle size of the electrode material, whereby improved contact among the electrode components achieved by milling contributed to enhancement of the capacity of an all-solid-state Li/S cell.

1. Introduction

Rechargeable Li-ion batteries are widely used as a power source for portable devices, and have recently attracted much attention as a large-scale power source for electric vehicles and hybrid electric vehicles. However, batteries for large-scale power applications require a much larger energy density. Elemental sulfur is considered to be one of the most promising candidates as a material for the positive electrode of a high-performance lithium secondary battery, because sulfur has a high theoretical specific capacity of 1672 mAh g^{-1} for the reaction with lithium to form lithium sulfide (Li_2S) [1,2]. However, the utilization of a sulfur electrode is not sufficient to achieve the theoretical capacity and rapid capacity fade is observed upon cycling of Li/S batteries using conventional organic liquid electrolytes [3–5]. This is caused by the high solubility of polysulfides, which are formed during both charge and discharge processes in liquid electrolytes [6,7]. In order to suppress the dissolution of polysulfides into the liquid electrolyte, various approaches such as the use of solid polymer [6,8] and ionic liquid-based electrolytes [9,10], and protection of the lithium anodes [11] have been examined. The capacity of a Li/S cell with a solid polymer electrolyte was improved by elevating the operation temperature to 100 °C; however, the cell still exhibited a low reversible capacity of less than 30% of the theoretical capacity of sulfur [8]. The low conductivity of solid polymer electrolytes could be one of the reasons for the poor capacity of such cells. However, inorganic solid electrolytes such as Li_2S–SiS_2 glass [12], Li_2S–P_2S_5 glass–ceramics [13,14] and thio-LISICONs in the $LiGeS_4$–Li_3PS_4 system [15] have exhibited high Li^+ ion conductivity of over 10^{-3} S cm^{-1} at 25 °C. Application of such inorganic solid electrolytes to a Li/S cell could eliminate the problem of polysulfide dissolution.

Several investigations of Li/S batteries using sulfide-based solid electrolytes have been carried out [16–19]. Sulfur is an ionic and electronic insulator. An all-solid-state cell with sulfur itself as an active material could hardly be charged and discharged, due to the insulative nature of sulfur; therefore to enable the electrochemical reaction between sulfur and lithium, a composite of sulfur and an electronically conductive material would be required. An all-solid-state cell using sulfur-based materials as a positive electrode and Li_2S–P_2S_5 glass–ceramics [16,17] or Li_2S–SiS_2 glasses [18] as a solid electrolyte exhibited excellent cycling performance with a large capacity at room temperature. A positive electrode consisting of sulfur and CuS was prepared by mechanically milling a mixture of sulfur and copper crystals. The use of sulfur in addition to CuS as an active material in the positive electrode of an all-solid-state cell have been previously suggested [16–18]. The mechanical milling of sulfur and copper proved to be effective in improving the electrochemical performance of an all-solid-state Li/S cell.

On the other hand, preparation of a composite of sulfur and a fine carbon material is an alternative approach to enhance the conductivity of sulfur. The energy density according to the electrode weight of Li/S cells would be increased by using fine carbon materials instead of metals such as copper. Various composite materials

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of sulfur and carbon have been used in Li/S cells with conventional liquid electrolytes [2,20–22]. Nazar and co-workers reported that the composite electrode of sulfur and mesoporous carbon exhibited an extremely high reversible capacity [2,22]. The pores of the mesoporous carbon were filled with sulfur by heating at temperatures higher than the melting point of sulfur, and thus an intimate contact between sulfur and carbon was formed, which led to improvement of the capacity and cyclability of the Li/S cells. Kanno and co-workers reported a composite material of sulfur and acetylene black (AB) prepared by gas-phase mixing that was applied as an electrode in an all-solid-state Li/S cell with a thio-LISICON crystalline solid electrolyte [19]. The formation of a favorable interface between sulfur and AB was reported to be essential to obtain a Li/S cell with high capacity; however, the cell operation was limited at low current density. The construction of not only an electron conducting path (AB) but also a Li^+ ion conducting path (solid electrolyte) to the active material (sulfur) is necessary for improvement of the performance in all-solid-state cells [23]. Improvement of the power and energy densities of all-solid-state Li/S cells is largely dependent on the success of an appropriate composite electrode design.

In order to prepare a good contact among the active material (sulfur), solid electrolyte (Li_2S–P_2S_5 glass–ceramic) and conducting additive (AB), composite electrode materials were prepared by mechanically milling these three component powders. The morphology of the composite electrode materials was investigated and they were then applied as positive electrodes of an all-solid-state cell. The secondary lithium battery cell performance was evaluated at temperatures from −20 °C to 80 °C under various current densities.

2. Experimental

Three different composite electrode materials with elemental sulfur as an active material were prepared by mortar grinding and ball-milling in a planetary ball mill apparatus (Fritsch Pulverisette 7) under an Ar atmosphere. The composite material consisted of sulfur (Aldrich, 99.998%), AB (Denki Kagaku Kogyo) and $80Li_2S{\cdot}20P_2S_5$ (mol%) glass–ceramic solid electrolyte (SE) in a weight ratio of 25:25:50. The $80Li_2S{\cdot}20P_2S_5$ glass–ceramic was prepared by a mechanochemical reaction process of Li_2S (Idemitsu Kosan Co., >99.9%) and P_2S_5 (Aldrich, 99%) as starting materials, with subsequent heat treatment at 210 °C for 1 h [14]. The $80Li_2S{\cdot}20P_2S_5$ glass–ceramic solid electrolyte exhibits favorable features for all-solid-state lithium cells such as high room temperature conductivity of *ca.* 10^{-3} S cm^{-1}, wide electrochemical window of over 10 V and high stability in contact with Li or Li–In alloy [24]. Three different composite electrode materials were prepared as follows: (a) (S + AB + SE), (b) (S – AB + SE), and (c) S – AB – SE. The (S + AB + SE) electrode was obtained by grinding sulfur, AB and SE with a mortar. The (S – AB + SE) electrode was obtained by milling the mixture of sulfur and AB using a planetary ball-mill apparatus and then grinding a mixture of the S–AB composite and SE using a mortar. The S–AB–SE electrode is obtained by milling the mixture of S–AB composite and SE. The following mechanical milling conditions were used: a zirconia vessel (45 ml) with 160 zirconia balls (5 mm diameter) was used with a fixed rotation speed of 370 rpm for 5 h. X-ray diffraction (XRD; M18XHF^{22}-SRA, MAC Science) measurements of the prepared materials were performed using Cu Kα to identify the crystalline phases. The morphology of the materials was evaluated by scanning electron microscopy (SEM; Jeol, JSM-5300).

The electrochemical properties of the sulfur-based electrodes were investigated using an all-solid-state cell. Two-electrode cells were fabricated using the sulfur-based electrode as a working electrode, the SE and a Li–In alloy as a counter electrode. The working electrode and SE were placed in a polycarbonate tube (10 mm diameter) and pressed together under 360 MPa. Li–In alloy was placed on the surface of the solid electrolyte side of the bilayer pellet and a pressure of 120 MPa was then applied to the three-layered pellet. The three-layered pellet was finally sandwiched using two stainless-steel rods as a current collector. All cell preparation processes were carried out in a dry Ar-filled glove box. Electrochemical tests were conducted at several constant current densities from 0.064 to 19.2 mA cm^{-2} at temperatures from −20 °C to 80 °C under an Ar atmosphere using a charge–discharge measurement device (BTS-2004, Nagano Co.).

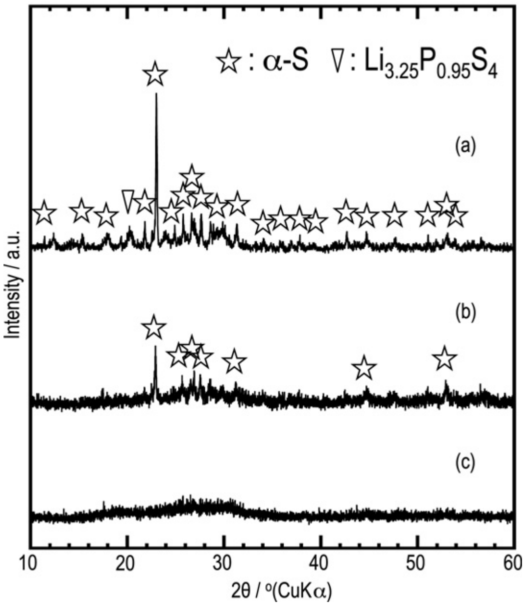

Fig. 1. XRD patterns of the (a) (S + AB + SE), (b) (S – AB + SE), and (c) S–AB–SE electrodes.

3. Results and discussion

Fig. 1 shows XRD patterns of the (S + AB + SE), (S – AB + SE), and S–AB–SE electrode materials. Diffraction peaks due to α–S with orthorhombic structure (JCPDS #078-1888) and the $Li_{3.25}P_{0.95}S_4$ crystal [14] precipitated in the SE were observed in the (S + AB + SE) electrode material. Milling the mixture of S and AB resulted in weakening of the peak intensity due to α–S. A halo pattern was observed for the S–AB–SE electrode material, which indicates that the sulfur in S–AB–SE became amorphous.

The morphologies of the S-based composite electrodes were investigated by SEM. SEM images of the (S – AB + SE) and S–AB–SE electrode materials are shown in Fig. 2. Two different particle types with sizes of 1–5 μm and 20–50 μm were observed in the prepared (S – AB + SE) electrode material (Fig. 2a). The particle sizes of the S–AB composites obtained by milling were 20–50 μm, which suggests that the 20–50 μm particles are the S–AB composite and the 1–5 μm particles are the SE. The S–AB–SE electrode material (Fig. 2b) forms agglomerates of less than 10 μm. Therefore, mechanical milling of the S–AB composite with the SE particles results in a decrease in the particle size of this sulfur-based electrode type.

Fig. 3 shows room temperature charge–discharge curves of the all-solid-state cells with the three types of sulfur-based electrodes at 0.064 mA cm^{-2}. The Li–In alloy was used as a counter electrode, because Li–In alloy exhibits a stable voltage plateau at 0.62 V vs Li/Li^+ in an all-solid-state cell with a sulfide solid electrolyte [25]. In