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Composite Sulfur Electrode Prepared by High-Temperature Mechanical Milling for use in an All-Solid-State Lithium–Sulfur Battery with a $Li_{3.25}Ge_{0.25}P_{0.75}S_4$ Electrolyte

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ABSTRACT

Composite sulfur electrodes are prepared by high-temperature mechanical milling (443 K) for use in all-solid-state lithium–sulfur batteries, and their structures and electrochemical properties are investigated. Composites comprising sulfur, acetylene black, and a $Li_{3.25}Ge_{0.25}P_{0.75}S_4$ solid electrolyte are fabricated by planetary ball milling using a temperature-controlled system. The composite electrode exhibits a high discharge capacity of greater than 1200 mAh g^{-1} and a good cycle capability. As a result of high-temperature milling, composites are formed, incorporating novel structural units from the reaction between sulfur and the solid electrolyte, along with their intrinsic characteristics. Hence, high-temperature milling demonstrates promise for the fabrication of a composite electrode exhibiting high, reversible electrochemical activities for use in an all-solid-state lithium–sulfur battery.

1. Introduction

Among the next-generation energy storage systems, lithium–sulfur (Li–S) batteries have attracted attention because of the high theoretical capacity of sulfur (1672 mAh g^{-1}) [1]. For this battery system, an all-solid-state configuration demonstrates promise because the dissolution of the intermediate products from discharging can be prevented by the replacement of the organic liquid electrolyte by lithium-ion conducting solids [2–4]. Typically, composite electrodes incorporating active materials (e.g., sulfur and lithium sulfide), electronic conductors (e.g., carbon and metal particles), and lithium-ion conducting solid electrolytes are used in all-solid-state Li–S batteries. Electronic conductors play an important role as electronic conduction pathways. In addition, they accommodate the volumetric changes of active materials [4–7]. On the other hand, solid electrolytes are considered to only serve as lithium-ion conduction pathways in the matrix. However, recent studies have revealed that the solid electrolytes can function as active materials in the composites prepared by long-time mechanical milling [8–10]. Therefore, the dual functions of solid electrolytes are believed to effectively improve the energy density of the Li–S battery system as the weight ratio of electrochemical active components in the composites noticeably increases by utilizing this design. Previously, $Li_2S-P_2S_5$-based materials have been reported to be activated by mechanical milling; batteries using these materials exhibit a specific capacity of greater than 150 mAh g^{-1} [9]. In addition, a novel electrode material of lithium polysulfidophosphate (Li_3PS_{4+n}), which has sulfur chain, has been synthesized by the solution reaction of sulfur and Li_3PS_4 using tetrahydrofuran [11]. Reversible discharge capacities over 300 cycles of Li_3PS_{4+n} were confirmed beyond 500 mAh g^{-1} at 333 K.

Recently, the feasibility of such activation for Li–Ge–P–S-based thio-LISICON material has been reported [10]. $Li_{3.25}Ge_{0.25}P_{0.75}S_4$ prepared by mechanical milling exhibits a low discharge capacity of less than 100 mAh g^{-1}, and a novel structural unit from the reaction between sulfur and $Li_{3.25}Ge_{0.25}P_{0.75}S_4$ during milling is obtained. However, this composite system, with sulfur, acetylene black, and the $Li_{3.25}Ge_{0.25}P_{0.75}S_4$ solid electrolyte, exhibits a relatively poor cycle capability as compared to those of $Li_2S-P_2S_5$-based systems,

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and the solid electrolyte is not effectively utilized. Nagao et al. have reported that a composite with increased cyclability and high energy density is obtained by high-temperature mechanical milling at 428 K [12]. Such high-temperature conditions may also contribute to material activation during milling. In addition, even though the electrochemical properties of a representative Li–P–S system are strongly dependent on its composition [13], high-temperature milling renders additional effects on the $Li_{3.25}Ge_{0.25}P_{0.75}S_4$ solid electrolyte. In this study, composite electrodes were fabricated using elemental sulfur as the active material, acetylene black as electronic conductive carbon [4,9], and a thio–LISICON ($Li_{3.25}Ge_{0.25}P_{0.75}S_4$) ion conductor as the solid electrolyte [14,15] by planetary ball milling using a temperature-controlled system. In addition, the structure, electrochemical properties, and reaction mechanism of the composite electrodes were investigated. Liquid-phase sulfur was used during milling as the additional effects caused by the atomic- or nano-level contact from sulfur in the liquid phase are expected [12]; these characteristics might contribute to the increased electronic or ionic conduction in the composites, resulting in high sulfur utilization and reversible battery reaction.

2. Experimental

A solid electrolyte powder (thio-LISICON, $Li_{4-x}Ge_{1-x}P_xS_4$ ($x = 0.75$)) was prepared by a solid-state reaction using Li_2S, P_2S_5, and GeS_2 as the starting materials [10,15]. Sulfur (Kojundo Chemical Laboratory Co., Ltd., 99.99% purity), acetylene black (AB; HS-100, Denka Co., Ltd.), and a solid electrolyte (SE) were weighed in a ratio of 25:25:50 (wt%), followed by mechanical milling using a planetary ball milling apparatus (LP-M2H, Ito Seisakusho Co., Ltd.). The S/AB/SE mixture was placed in a zirconia ball-milling pod with zirconia balls (3 mm-ϕ × 90 and 5 mm-ϕ × 45) in an Ar-filled glove box and then mixed at 480 rpm. Various milling times (10–600 min) and milling temperatures (298–443 K) were examined. The structure of the composites and the electrochemical properties of the all-solid-state batteries were evaluated by scanning electron microscopy (SEM), Raman spectroscopy, and galvanostatic charge–discharge tests. Thermogravimetric analysis (TGA; Rigaku Thermo plus TG8120) of sulfur was performed to determine the milling temperature. An inert Ar atmosphere was used for TG/DTA measurements, and the samples were heated from 298 to 473 K at 5 K min^{-1}.

The morphologies of the composite electrode were observed by SEM (JSM-6610LV, JEOL) with an accelerating voltage of 5–20 kV. The composites were transferred from an Ar-filled glove box to the SEM observation room in an Ar-filled container to prevent the exposure of the sample from air. Raman spectroscopy measurements were performed using the composite electrode on a confocal Raman microscope (Raman 11, Nanophoton Corp.) with an excitation wavelength of 532 nm. All the specimens for Raman spectroscopy were prepared in an Ar-filled glove box. An appropriate amount of the powder was sealed in a glass capillary (0.2–0.3 mm in diameter) under ambient pressure using vacuum grease. After the sample preparation, the specimen was withdrawn from the glove box, and the glass capillary was exposed to ambient air for less than 1 h for all the measurements. The composite electrodes were also characterized by thermogravimetric (TG) measurement (Rigaku Thermo plus TG8120). For the TG measurements, the specimens were first exposed to ambient sir for a short time (less than 1 min), and then heated in inert argon gas from 298 to 750 K at 5 K min^{-1}.

The all-solid-state batteries were constructed in an Ar-filled glove box for charge–discharge measurements. Solid electrolyte of $Li_{3.25}Ge_{0.25}P_{0.75}S_4$ powder (70 mg) was pressed into a pellet at 280 MPa as a separator layer. Pressing was performed using a test cell, with a polyethylene terephthalate (PET) cylinder body having an inner diameter of approximately 10 mm. Subsequently, 5 mg of the composite electrode powder (as the cathode) with an Al current collector was pressed onto one side of the solid electrolyte at 700 MPa. A Li–In alloy anode ($\approx$0.6 V *vs.* Li/Li^+) [16] was used in this study; lithium (thickness: 0.1 mm; diameter: 5 mm) and indium (thickness: 0.1 mm; diameter: 10 mm) foils with a Cu current collector were pressed at 17.6 MPa on the opposite side as the counter or reference electrode.

Electrochemical properties of the cells were investigated by galvanostatic charge–discharge measurements using a multichannel galvanostat (TOSCAT-3100, Toyo System Co., Ltd.). The cutoff voltages for discharging and charging were 0.73 and 2.4 V, respectively, versus the Li–In alloy anode. A constant current of 83.75 mA g^{-1} (1/20C) was applied for charging and discharging with a rest time of 1 h at the charged and discharged states. The current value was calculated on the basis of the nominal sulfur content (25 wt% in the composite). Electrochemical tests performed at 298 K started at discharging.

3. Results and discussion

3.1. Electrochemical properties of the composites prepared by high-temperature milling

Fig. S1 shows the differential thermal analysis (DTA) curve of sulfur powder. Three endothermic peaks were observed at around 379, 391, and 451 K, corresponding to the phase transition from α- to β-sulfur, melting of sulfur, and evaporation of sulfur, respectively [17]. As liquid sulfur, exhibiting low viscosity especially at around 430 K, can provide increased contact with the solid electrolyte and acetylene black during milling, a temperature of 423 K was selected [12,18]. Fig. 1 shows the charge–discharge curves and Coulombic efficiency of the batteries using the composite electrodes prepared by high-temperature milling, and Fig. 2 shows the discharge capacities and capacity retention. The batteries exhibited a high discharge capacity of greater than 1000 mAh g^{-1} and an average reaction voltage of lithium and sulfur around 1.5 V versus a Li–In anode [12,13]. In addition, a high discharge capacity of greater than 1000 mAh g^{-1} was still maintained at the 20th cycle, thus confirming the enhancement in electrochemical performance by high-temperature milling; the composite prepared at room temperature exhibited a low discharge capacity of less than 680 mAh g^{-1} [10]. At the 1 st cycle, the charge capacity of the composite electrode exceeded the discharge capacity; thus, increased amounts of lithium are extracted from the composite than that inserted. This unique behavior is also confirmed by the Coulombic efficiency, as Fig. 1(b) shows an efficiency over 100% at the 1st cycle. These results indicated that the solid electrolyte contributes to the battery reaction [8–10]. In addition, the discharge capacities at the 2nd cycle significantly increased, revealing that the solid electrolyte activated at the 1 st cycle continues to contribute to the battery reaction in the following cycles [19]. The composite exhibited higher discharge capacity (>800 mAh g^{-1}) and higher capacity retention of approximately 80% after the 40th cycle as compared with those reported previously for composites incorporating sulfur, acetylene black, and the $Li_{3.25}Ge_{0.25}P_{0.75}S_4$ solid electrolyte [4,10]. The relatively high Coulombic efficiency during cycling also supports enhanced electrochemical performance of the composite electrode.

In summary, high-temperature mechanical milling is confirmed to form a composite with electrochemical properties better than those of the composite prepared by mechanical milling without heating and/or gas-phase mixing processes [4,10]. Hence, high-temperature milling contributes to the high capacity and cycle