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Characterization of sulfur nanocomposite electrodes containing phosphorus sulfide for high-capacity all-solid-state Na/S batteries

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ABSTRACT

All-solid-state Na/S cells with high safety, capacity, and low material costs are desirable for smart grid systems. We report sulfur composite electrodes prepared by the mechanical milling of sulfur, Ketjen black, and P_2S_5 or Na_3PS_4 for high-capacity cells. A cell using P_2S_5, which is not ion conductive, in the sulfur electrode exhibits a high reversible capacity of 340 mAh (g-sulfur electrode)$^{-1}$ at 0.04 C rate at 25 °C, which is much larger than that (37.3 mAh (g-sulfur electrode)$^{-1}$) obtained in a conventional cell using a high ion-conductive Na_3PS_4 electrolyte. To investigate the reaction mechanism of the sulfur composite electrode containing P_2S_5, X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) measurements and scanning and transmission electron microscopy (SEM/TEM) observations of the electrodes were conducted. The results indicate that a crystalline Na_3PS_4 component is automatically produced by the electrochemical reaction with Na in the amorphous S-P_2S_5 electrode and it mixing with the sulfur redox parts at the nanoscale. The mixing degree is higher than that at microscale in the conventional S-Na_3PS_4 electrode, which results in the high capacity of the cells containing the S-P_2S_5 electrode. Partial substitution of P_2S_5 for SiS_2 in the sulfur electrode suppresses the nanocrystallization and further increases the reversible capacity up to 390 mAh (g-sulfur electrode)$^{-1}$ under 0.04 C rate, which is the highest in reported all-solid-state Na batteries to date.

1. Introduction

Energy storage batteries with high capacity are key devices to solve the global energy deficit. Sulfur, as an electrode active material, has a high theoretical capacity of 1672 mAh g^{-1} and is expected to be a high capacity electrode material in lithium, sodium, and magnesium batteries [1]. However, the discharged intermediates, polysulfide ions ($S_{8-x}{}^{2-}$ ($0 \leq x \leq 4$)), dissolve in conventional organic electrolyte solutions such as tetraethylene glycol dimethyl ether. The dissolution of the active materials causes a decrease in the cell capacity and continuous reduction of the discharged products because of their migration to the negative electrode (shuttle phenomenon) [2], thus wasting the charging energy. In addition, these conventional organic electrolyte solutions have risks of the leakage and ignition [3]. Bulk-type all-solid-state batteries using solid electrolytes instead of those electrolyte solutions are expected to solve the dissolution and safety problems [4,5]. Solid electrolytes with high ionic conductivity are needed for these batteries. Sulfide electrolytes such as $Li_{10}GeP_2S_{12}$ crystal [6] and $70Li_2S{\cdot}30P_2S_5$ glass-ceramic [7] show high ionic conductivities comparable to those of organic electrolyte solutions. These solid electrolytes are usually mixed to form the ionic conductive pathways to sulfur in the electrodes. A homogeneous dispersion is considerably important for the performance of these batteries because the sulfur active materials act as insulators during the discharge-charge processes [8,9]. We have reported that mechanical milling increases the mixing degree and the capacity based on a weight of the sulfur active material from 250 to 1220 mAh (g-sulfur)$^{-1}$ in all-solid-state Li/S batteries [10]. However, the content of the sulfur active material in the composite electrode is only 25 wt% and the current density of 0.064 mA cm^{-2} (0.01 C) is still low. Furthermore, increasing the sulfur active material content in the composite electrode to obtain a higher cell capacity drastically decreases the utilization of sulfur and the rate performance in the cells because of the lower conductivity of the electrode [11,12,13]. Recently, Nagata *et al.* reported that an all-solid-state Li/S cell with a high sulfur content of 60 wt% in a sulfur composite electrode exhibit a high reversible capacity of about 1220 mAh (g-sulfur)$^{-1}$ at a relatively high

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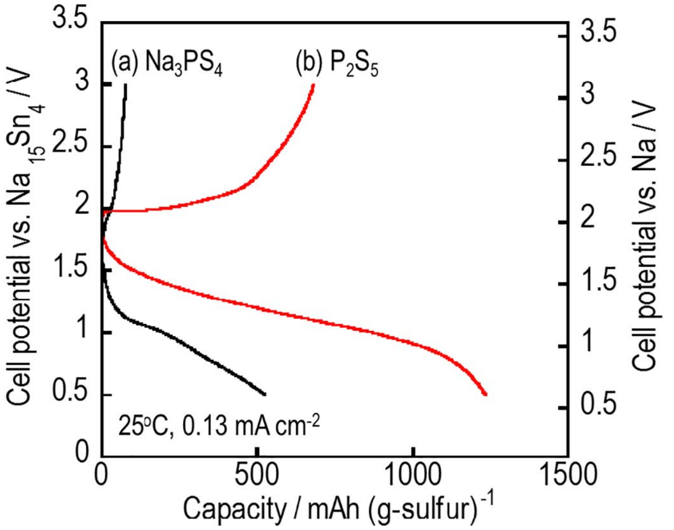

Fig. 1. The 1st discharge–charge curves of the all-solid-state Na/S cells with a sulfur composite electrode of S-KB-Na_3PS_4 (a) or S-KB-P_2S_5 (b) at 25 °C at a current density of 0.13 mA cm^{-2}.

current density of 1.6 mA cm^{-2} (0.5 C) [14]. The areal loading of a sulfur active material was 3.5 mg cm^{-2}. In these cells with high capacity and rate performance, P_2S_5 was used as the solid electrolyte component to the sulfur composite electrode. The reversible capacity per weight for the positive electrode of 732 mAh (g-electrode)$^{-1}$ is the highest of reported all-solid-state cells to date. The discharge–charge mechanism of the sulfur electrode containing P_2S_5 seems to be different from that of sulfur electrodes containing an ionically conductive solid electrolyte because P_2S_5 itself has no ionic conductivity. We have previously characterized the structure of the sulfur composite electrode (S-P_2S_5-C) and proposed the reaction mechanism [15]. The mechanical milling treatment produces amorphous P_2S_{5+x} species with phosphorus atoms bridged by sulfur chains. The cleavage and formation of disulfide bonds in the amorphous compounds are brought about by the discharge and charge process, respectively. Both sulfur redox parts and ionic conductive parts derived from P_2S_5 compound are formed and mixed at the atomic level during the discharge–charge processes. We have suggested that the favorable dispersion of the electrode components is one reason for the high capacity of the all-solid-state Li/S batteries using P_2S_5 in the sulfur composite electrode. Nagata *et al.* reported that all-solid-state Na/S batteries with a high sulfur content of 50 wt% in the sulfur composite electrodes containing P_2S_5 also show higher capacities than those using a Na_3PS_4 glass-ceramic electrolyte [13,16] with a high ionic conductivity [17]. Although the initial discharge capacity is 1450 mAh (g-sulfur)$^{-1}$, the reversible capacity is 670 mAh (g-sulfur)$^{-1}$, which is lower than that of the all-solid-state Li/S batteries. However, the usage of sodium is better than that of lithium on a strategy using abundant chemical elements [18]. It is also interesting to clarify the difference in the electrochemical reactions of the sulfur composite electrode in Na/S batteries from those in Li/S batteries. Gel-polymer electrolytes have also been used for Na/S batteries because they are an another good direction to reduce the potential of the fire hazard [19–21] However, these Na/S batteries showed small reversible

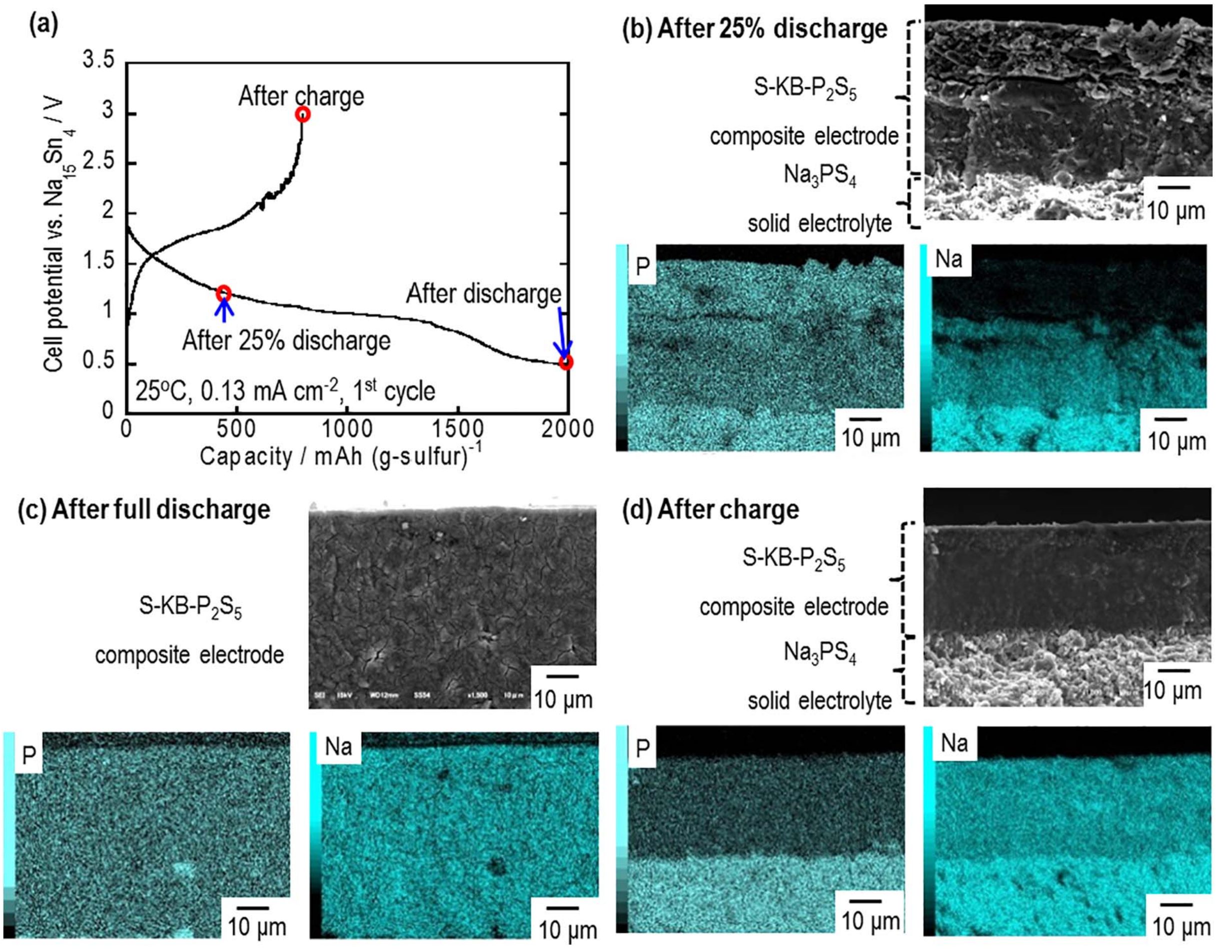

Fig. 2. (a) The 1st discharge–charge curves of the all-solid-state Na/S cells with a sulfur composite electrode of S-KB-P_2S_5 with a S:KB:P_2S_5 weight ratio of 45:19:36 at 25 °C at a current density of 0.13 mA cm^{-2}. SEM and EDX mapping images of a cross-section of the S-KB-Na_3PS_4 composite electrode after 25% (b) and full (c) discharge and charge (d) processes.