Li₂S nanocomposites underlying high-capacity and cycling stability in all-solid-state lithium-sulfur batteries

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Abstract

All-solid-state sulfur-based rechargeable lithium batteries have been expected to have superior energy density and high reliability so far. In general, the solid-solid interface between electrode and electrolyte particles has strong influence on the cell performance. Recently it is realized that all-solid-state lithium-sulfur batteries exhibit good cycling performance by reducing the particle size down to submicron scale. However, the origin of excellent reversibility has not been understood. Here we clearly demonstrate Li_2S nanocomposites underlying high-capacity and cycling stability in all-solid-state lithium-sulfur batteries. Through high-resolution transmission electron microscopy (TEM) and energy-dispersed X-ray (EDX) spectroscopy experiments, reversible structural and morphological changes at the nanoscale during the full-electrochemical cycles in next-generation all-solid-state lithium-sulfur batteries have been revealed for the first time. Reversible variations during cycles between crystallization and amorphization of sulfur-based active nanoparticles are responsible for the feasibility of the high capacity and cycling stability. The smooth and adhesive interface between them is truly realized at the nanoscale, which is fabricated by mechanical milling technique. Our experimental findings will lead to new route to generate the sulfur-based rechargeable batteries with high-capacity and cycling stability.

Keywords: lithium-sulfur battery, all-solid-state battery, positive electrode, sulfide electrolyte, TEM, nanocomposite

1. Introduction

Rechargeable lithium-ion batteries have been widely used in portable electronic equipments such as cellular phones and personal computers [1,2]. Increasingly they are also being scaled up for using large applications in electric vehicles and smart grids [3]. However, due to limited capacity in both positive and negative electrodes, the specific energy density of lithium-ion batteries need to improve remarkably to meet the requirements for practical applications [4]. Current positive electrode materials have an actual capacity less than half that of negative electrode materials such as graphite and silicon. Therefore, high-capacity positive electrode materials are required to realize lithium-ion batteries with higher-energy densities.

Lithium sulfide, Li_2S , is a high-capacity positive electrode material with the theoretical capacity of 1168 mAh g^{-1} , which is four times higher than those of LiCoO_2 and LiFePO_4 positive electrodes [5,6]. However, there are two major issues to be solved. One is that its low electronic conductivity restricts its actual capacity to much lower values than that theoretically predicted [7]. The other is capacity fading which arises from high dissolution of lithium polysulfide into the liquid electrolyte during the electrochemical reaction of Li_2S electrode [8]. The use of inorganic solid electrolyte (SE) is expected to inhibit the polysulfides dissolution. We reported that a Li_2S -Cu

composite electrode prepared by mechanical milling retained the reversible capacity of 350 mA h g^{-1} for 20 cycles in all-solid-state cells using $\text{Li}_2\text{S-P}_2\text{S}_5$ SEs [9,10]. Recently it is found that Li_2S electrode prepared by milling exhibited excellent cycling stability with high capacity of 700 mAh g^{-1} in the all-solid-state cells [11]. Furthermore, TEM observation of the Li_2S electrodes in the all-solid-state cells revealed that intimate contacts among submicron Li_2S active material, acetylene black (AB) and the $\text{Li}_2\text{S-P}_2\text{S}_5$ SE particles were retained for 10 cycles, which is mainly responsible for excellent cell performance [11]. Because of the large volumetric expansion and contraction of active materials during cycling, the cell performance should depend strongly on the retention of the electrode/electrolyte interface during charge-discharge cycle. It has not been clear whether the submicron Li_2S should serve as the active materials retaining excellent contact with the SE and AB upon cycling and contribute mainly to the satisfactory cell performance such as cycling stability and high capacity.

On the other hand, it is important to understand the reaction mechanism upon cycling in Li_2S electrode to realize the excellent cell performance. However, few studies have been done about the reaction mechanism in the Li_2S electrode in the lithium-sulfur batteries [12-14]. In the case of the all-solid-state cells containing the Li_2S electrode, Takeuchi *et al.* proposed that the electrochemical reaction $\text{Li}_2\text{S} \leftrightarrow 2\text{Li} + \text{S}$ proceeded,

based on S K-edge XAFS experiments [12]. However, both the morphology and the structure of reaction products have not been clear so far. In order to clarify the reaction mechanism, it is indispensable to get detailed information on the nanoscaled morphology of the electrode and the nanostructures of active materials in the electrode simultaneously.

In this article we report microstructural changes, morphological evolution and reaction processes in the ball-milled Li_2S electrode of all-solid-state lithium-sulfur cells during charge-discharge cycles. Using high-resolution TEM, electron diffraction (ED) and EDX spectroscopy experiments, we clearly demonstrate the presence of the nanoscaled crystalline Li_2S particles involved in the amorphous SE and reversible conversion between amorphization and crystallization upon cycling. Based on the experimental results, the reaction mechanism at the interface between SE and positive electrode will be discussed. Our experimental findings will offer new insight into a route for developing high-performance of all-solid-state lithium-sulfur batteries.

2. Experimental

Li_2S (Idemitsu Kosan, >99.9%), acetylene black (AB, Denki Kagaku Kogyo) and $75\text{Li}_2\text{S}\cdot 25\text{P}_2\text{S}_5$ (mol%) glass solid electrolyte (SE) were used as starting materials. The

SE was obtained via mechanical milling process [15], and was found to be amorphous by X-ray diffraction measurement. The Li_2S composite electrodes of Li_2S , AB and the SE with the weight ratio of 25:25:50 were prepared by mechanical milling with a planetary ball-mill apparatus. The following mechanical milling conditions were used. A ZrO_2 pot with 100 ZrO_2 balls was used. Li_2S particles were milled for 20 h at a rotation speed of 510 rpm. A mixture of the Li_2S particles and AB was milled and then the electrodes were obtained by milling a mixture of the Li_2S -AB composite and the SE. The rotation speed in both the processes was fixed at 370 rpm for 1 h.

The all-solid-state electrochemical cells $\text{In}/\text{Li}_2\text{S}$ were fabricated using the obtained Li_2S composite electrodes as the working electrode, the $75\text{Li}_2\text{S}\cdot 25\text{P}_2\text{S}_5$ glass as the SE and an indium foil as the counter and reference electrodes. The working electrode (10 mg) and the SE (80 mg) powders were placed in a polycarbonate tube (diameter: 10 mm) and pressed together at a pressure of 360 MPa. Indium foil (46 mg) was put on the surface of the SE side of the bilayer pellet and a pressure of 240 MPa was applied to the pellet. The three-layered pellet was sandwiched between two stainless-steel rods as current collectors. All the processes were carried out in an Ar-filled glove box. The electrochemical tests of the cells were carried out at a constant current density of 0.064 and 0.13 mA cm^{-2} at 25°C in the voltage range from 0 to 3 V under an Ar atmosphere

using a charge-discharge measuring device (Nagano, BTS-2004).

X-ray diffraction (Rigaku, Ultima IV) measurements on the Li_2S electrode in all-solid-state $\text{In}/\text{Li}_2\text{S}$ cells were performed to analyze the structure in the pristine electrode and subsequently in the electrodes after the first charge and discharge, and the 20th discharge. The cross-section of a bi-layer of the Li_2S electrode and the SE was prepared by an ion-milling technique for SEM observation. High-resolution TEM observation of the Li_2S electrode was carried out for the pristine electrode and in the electrodes after the initial charge and discharge, and after the 20th discharge. Prior to TEM observation, the cell was disassembled, Li_2S electrode was scratched, and then the obtained powders were placed on a grid for TEM observation without any artificial damage. These samples were placed in a folder to maintain inert atmosphere, and then were transferred to TEM apparatus (JEOL, JEM-2100F) equipped with energy-dispersive X-ray spectroscopy.

3. Results and discussion

Li_2S composite electrodes consisting of Li_2S active materials, acetylene black (AB) and $75\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5$ (mol%) glass SEs [15] were prepared by mechanical milling, and we applied cold pressing method at room temperature to fabricate three-layered powder

compressed pellet of indium (counter and reference electrodes)/75Li₂S·25P₂S₅ glass SE/Li₂S (working electrode). In order to observe the morphology of the electrode layer and the electrode-electrolyte interface clearly, cross-section of a bi-layer of the Li₂S electrode and the SE was prepared by an ion-milling technique. Figure 1a shows the cross-sectional SEM image of the bi-layer. The brightest (white) grains are SEs, darkest (black) grains are AB and the intermediate gray contrast is the region where Li₂S, AB and the SE are well mixed by mechanical milling. The gray contrast is observed in large areas of the electrodes, meaning that enough conducting paths of electrons and lithium ions to Li₂S active materials are formed in the electrode. Figure 1b shows the magnifying image of the rectangle region of Figure 1a. The smooth and adhesive contacts between the Li₂S electrode layer and the SE layer are constructed by cold pressing as shown in Figure 1b.

The electrochemical properties of the all-solid-state cells using the Li₂S electrode were examined. The charge-discharge curves (Figure 1c) and cycle performance (Figure 1d) of the cells In/Li₂S are shown. The cell was initially charged (extraction of lithium ion from Li₂S active material) and subsequently discharged (insertion of lithium ion into Li₂S active material) at 25 °C. The cell has the initial charge capacity of 900 mAh g⁻¹ and the discharge capacity of 620 mAh g⁻¹ with the average operating potential of about

2 V vs. Li, as displayed in Figure 1c. Coulombic efficiency of the cell is 99 ~ 100% from the 3rd to 10th cycles, although the initial efficiency is a lower value, 69%. The cell exhibits a good cyclability with high capacity of 450 mAh g⁻¹ for 20 cycles at 0.064 mA cm⁻² and 0.13 mA cm⁻². The capacity is three times higher than that of current layered metal oxide and phosphate positive electrodes.

To explore the reaction mechanism of the all-solid-state In/Li₂S cells, ex-situ X-ray diffraction measurements on the Li₂S electrode were performed in the pristine electrode and subsequently in the electrodes after the initial charge and discharge, and the 20th discharge. Figure 1e clearly shows changes of the crystal structures from the crystalline Li₂S active materials to the amorphous Li₂S during the cycling. Note that in the X-ray diffraction profile of the pristine electrode, all the diffraction peaks were indexed by the cubic structure (space group; *Fm-3m*) [16], which should stem from the crystalline Li₂S active material. In addition, a halo pattern derived from 75Li₂S·25P₂S₅ glass SE can be detected. After the initial charge, the peak intensities due to the cubic structure of Li₂S drastically decrease and, on the other hand, a new broad profile appears at around 2θ=22°, where the peak intensity of crystalline sulfur is the highest. This result implies that the crystalline Li₂S changes into amorphous sulfur. After the initial discharge, the broad profile due to amorphous sulfur disappears and there is no significant change in

the peaks due to the crystalline Li_2S . From these results, it is suggested that amorphous sulfur should react with lithium ion to form amorphous lithium polysulfide (Li_2S_x , $1 \leq x \leq 8$), although the existence of Li_2S_x has not been confirmed by XRD. The peaks due to the crystalline Li_2S disappear completely after 20 cycles, as understood in Fig. 1e. The XRD profile after 20 cycles almost coincides with that after the initial discharge. These results imply that the following electrochemical reaction proceeds reversibly after the 2nd cycle: amorphous $\text{Li}_2\text{S}_x \leftrightarrow$ amorphous sulfur.

In order to clarify morphology in Li_2S electrode at the nanoscale and its reaction mechanism, we carried out high-resolution TEM observation on the electrode in the cells. Before cycling, both high-resolution TEM images (Figure 2a) and ED patterns (Figure 2b) reveal that nano-particles with different crystal orientations distributed randomly in the matrix consisting of amorphous SE and AB. Their average sizes of the nano-particles can be estimated to be approximately 5 nm. To identify the nano-particles found in the high-resolution TEM image, lattice parameters were calculated from the intensity peaks labeled by the asterisks in Figure 2c; the estimated lattice parameter of 0.571 nm is almost identical with that of the crystalline Li_2S [16]. Note that Figure 2c shows the intensity profile obtained along the dotted line in the ED pattern of Figure 2b and Q (= 0) in Figure 2c corresponding to the center of the ED pattern. These imply

that, since $75\text{Li}_2\text{S}\cdot 25\text{P}_2\text{S}_5$ glass SE consists of Li^+ and PS_4^{3-} , crystalline Li_2S can be regarded as only Li_2S active material. On the other hand, dark-field image (not shown here) obtained using the diffraction spot due to the crystalline Li_2S electrode clearly revealed that the crystalline Li_2S active material with the size of about 5 nm is well dispersed, in addition to a scatter of the particles with the size larger than 50 nm. This morphology comprising the Li_2S nano-particles, SE and AB should play a crucial role in the high capacity of the all-solid-state lithium-sulfur cells.

Another striking phenomena found in this work is the reversible structural changes between the crystalline nano-particles and the amorphous structure upon cycling. To elucidate changes of the microstructures during the charge process, high-resolution TEM observation was performed in the Li_2S electrode after the 1st charge. As shown in Figure 2d no lattice fringes due to the crystalline Li_2S can be seen and there exists the characteristic contrast due to amorphous structure in the whole region. In the ED pattern and the intensity profile of Figures 2e and 2f, only halo pattern can be seen. Considering the X-ray diffraction profiles in Figure 1e, the amorphous sulfur should result in the halo pattern. On the other hand, significant phenomena in the understanding of the good capacity retention with high capacity were found in the samples after the 1st and the 20th discharge performance. As shown in Figures. 2g and 2j, lattice fringes with spacing

of about 3.9 Å are clearly seen in high-resolution TEM images at the 1st and 20th discharge stage, suggesting that amorphous sulfur is converted into crystalline nanoparticles during discharge reaction. Both the crystalline sizes are about 5 nm, which is almost consistent with that in the pristine electrode of Figure 2a. On the other hand, significant features in ED patterns of Figures 2h and 2k were found. One of the features is the appearance of the Debye-Scherrer rings due to the nano-particles with randomly distributed crystal orientations and the other is the presence of the diffraction spots originating from the crystalline particles. The Debye-Scherrer rings results from the crystalline Li_2S nanoparticles. On the other hand, the diffraction spots indicated by arrows in Figures 2h and 2k should stem from the crystal structure of lithium polysulfide. It should be noticed that conventional X-ray diffraction experiment could not detect the reflection peaks due to the Li_2S crystallines with the size less than 5 nm, while high-resolution TEM experiments revealed the existence of crystalline Li_2S nanoparticles. From careful analysis of the ED patterns in Figures 2h and 2k, lattice parameters calculated from the reflection spots indicated by arrows are estimated to be about 3.89 Å, which correspond to those of Na_2S_2 and Na_2S_4 . Unfortunately to the best of our knowledge, the crystal structure and lattice constants of lithium polysulfide such as Li_2S_2 or Li_2S_4 have never been reported so far. If sodium sites in a sodium

polysulfide would be replaced for lithium, discharge reaction product could be identified as lithium polysulfide. These results suggest that the reversible reaction of $\text{Li}_2\text{S} \leftrightarrow \text{S} + 2\text{Li}^+ + 2\text{e}^-$ proceeds in Li_2S particles with the smaller size (less than 10 nm), and irreversible reaction occurs in the particles with larger size (50 ~ 200 nm): charge reaction of $\text{Li}_2\text{S} \rightarrow \text{S}$ and discharge reaction of $\text{S} \rightarrow \text{Li}_2\text{S}_2$ or Li_2S_4 occurs.

Figures 3a and 3b respectively show high-resolution TEM image and EDX line profile of Li_2S electrode after the 1st charge. EDX analysis was carried out on the line (25 nm in length) in the high-resolution TEM image. Here we focused on the two particles, which are labeled as ① and ②, respectively. The EDX intensity due to sulfur element in the particle ② is much stronger than that in the particle ① and, on the other hand, the EDX intensity due to carbon element in the particle ② is much weaker. These indicate that the particle ① corresponds to AB particle, and the particle ② can be identified as compound consisting of Li_2S active material and AB. The EDX intensity due to phosphorus element remains intact in the two particles ① and ②. Li_2S - P_2S_5 SE is distributed homogeneously in the electrode because the volume of the SE is larger than that of Li_2S active material. EDX analysis of individual particles revealed that intimate contact among Li_2S active material, AB and Li_2S - P_2S_5 SE is retained on the nanometer scale.

Based on these ex-situ XRD and high-resolution TEM experiments of Li_2S electrode in all-solid-state $\text{In}/\text{Li}_2\text{S}$ cells, its reaction mechanism could be proposed as follows, as shown schematically in Figure 3c. Before charge-discharge cycling, Li_2S active material is present with at least two different sizes: nanoparticles less than 10 nm and larger sized particles (50 ~ 200 nm). Both Li_2S completely change to amorphous sulfur at the 1st charge process. At the 1st discharge process, amorphous sulfur derived from Li_2S nanoparticles forms crystalline Li_2S with the size less than 10 nm, while that derived from Li_2S with a larger size results in intermediate crystalline Li_2S_x . The reaction processes at each step are as follows:

<1st charge>

<1st discharge & subsequent cycles from 2nd cycle>

Let us discuss their origin of high-capacity and cycling stability in all-solid-state lithium secondary batteries consisting of $\text{In}/\text{Li}_2\text{S}-\text{P}_2\text{S}_5 \text{ SE}/\text{Li}_2\text{S}$. It is well known that Li_2S has a low lithium ion diffusion coefficient [14], in addition to a low electronic

conductivity and Li_2S undergoes the large volumetric expansion and contraction during cycling. The dissolution of lithium polysulfide species into a liquid electrolyte is also a reason for capacity fading. It is recognized that capacity and cycling stability are insufficient in conventional liquid-type cells using Li_2S electrode [8]. The initial charge and discharge capacities are respectively *ca.* 1,600 and 370 mAh g^{-1} and the initial Coulombic efficiency is 23%. The charge and discharge capacity decreases respectively to *ca.* 700 mAh g^{-1} and 350 mAh g^{-1} and the efficiency is 50% at the 10th cycle. We demonstrate here the unprecedented good cell performance in all-solid-state lithium-sulfur cells, as shown in Figures 1c and 1d. Coulombic efficiency of the all-solid-state cell is almost 100% after the initial two cycles. Highly adhesive electrode/electrolyte interface should play a crucial role in the cell performance. Because Li_2S active materials with the size less than 10 nm were surrounded by the AB and SE particles in the pristine electrode, electron and lithium ion conduction paths to the Li_2S active material are realized and diffusion distance of lithium ion is shorten within the Li_2S nanoparticles. These morphologies of the electrolyte/electrode lead to the achievement of high utilization of Li_2S at the initial charge process.

Focused on the initial discharge process, two distinct reaction processes were found depending on the Li_2S particle sizes. One is a reversible reaction by the conversion

between nanosized crystalline Li_2S and amorphous sulfur which proceeds in the active materials less than 10 nm. The other is the conversion from amorphous sulfur to lithium polysulfides (Li_2S_2 or Li_2S_4) with the size larger than 50 nm. The latter reaction results in the irreversible capacity at the initial cycle because those lithium polysulfides, in which a diffusion pathway is longer, are difficult to utilize completely as an active material. To enhance the reversible capacity in the all-solid-state lithium-sulfur cells at the initial cycle, it should be indispensable that the Li_2S nanoparticles less than ~10 nm in size are well dispersed in the matrix consisting of AB and SE particles.

The excellent cycling stability during 20 cycles is due to the fact that there were little changes of the morphologies of the Li_2S electrodes at the initial discharge (Figure 2g) and at the 20th discharge states (Figure 2j). The significant point to be considered is that the uniform dispersion of the Li_2S nanoparticles in the AB and SE matrix remains intact during cycling without their agglomeration. This is because the Li_2S - P_2S_5 SE would play a key role in suppressing the volumetric change of Li_2S active materials. As shown in Figures 1a and 1b, the SE was significantly densified by applying the cold pressing method at room temperature. Therefore, it is considered that Li_2S - P_2S_5 SE, which is flexible and has favorable elastic properties, works effectively as an inhibition of the volume change of the electrodes.

4. Conclusions

We succeeded in observing the crystalline Li_2S nanoparticles, retaining contact with the SE and AB particles, by high-resolution TEM and EDX experiments. The crystalline Li_2S nanoparticles are decomposed into the amorphous sulfur by the delithiation. On the other hand, subsequent lithiation induces the crystallization of both Li_2S in active materials less than 10 nm in size and lithium polysulfides larger than 50 nm in size. The Li_2S particles with the size less than 10 nm are used reversibly as an active material. The structural reversibility of Li_2S nanoparticles result in good cycling stability with high capacity for 20 cycles. The control of the smooth solid-solid interface between electrolyte and electrode and miniaturization of the active particles at the nanoscale will lead to the realization of the new-generation sulfur-based batteries in the near future.

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Figure 1 (a) Cross-sectional SEM image showing the interface between solid electrolyte (SE) and the composites of Li₂S, AB and SE glass and (b) magnifying image of its rectangular region (a). (c) Initial charge-discharge curves of all-solid-state cells consisting of In / 75Li₂S·25P₂S₅ glass SE / Li₂S at 0.064 mA cm⁻² at 25°C. (d) Cycle performance of the cells at 0.064 mA cm⁻² during the first ten cycles and at 0.13 mA cm⁻² after the eleventh cycle. (e) X-ray diffraction profiles of Li₂S composite electrode before cycling, after initial charge, after initial discharge and 20th discharge.

Figure 2 Morphological observation of Li_2S -based electrodes at nano-scale and their reaction mechanism. (a, d, g, j) High-resolution TEM images, (b, e, h, k) electron diffraction patterns and (c, f, i, l) their intensity profiles of Li_2S electrode (a-c) before cycling, (d-f) after initial charge, (g-i) after initial discharge and (j-l) after the 20th discharge.

Figure 3 EDX line profile of Li_2S -based electrodes and summary of the model for the structural and morphological changes of the electrodes during cycling. (a) High-resolution TEM images showing the excellent interfacial contact among Li_2S active material, AB and Li_2S - P_2S_5 SE. (b) EDX line profiles obtained along the solid line in (a). (c) Schematic description of proposing the reaction mechanism of Li_2S -based electrode in next generation all-solid-state Li/S batteries. The yellow background of these images shows solid electrolyte.