An All-solid-state Lithium Battery with Sulfur as Positive Electrode Materials

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An all-solid-state lithium battery was assembled with sulfur as positive electrode materials and with an inorganic solid electrolyte a-$60Li_2S{\cdot}40SiS_2$ (mol %). The all-solid-state lithium battery showed successive reversibility with large specific capacity. The specific capacity calculated on the base of the mass of sulfur was more than $1000\,mA{\cdot}h{\cdot}g^{-1}$.

Electrode materials with large specific capacity are strongly desired for developing and upgrading high-energy-density lithium batteries, because there are the increasing social demands for more efficient consumer batteries and propulsion of electric vehicle.[1] Elemental sulfur is very attractive as the positive electrode materials for the high-energy-density lithium batteries because of its large theoretical specific capacity of $1670\,mA{\cdot}h{\cdot}g^{-1}$. In addition, the elemental sulfur has the advantages of nontoxicity and inexpensiveness.

Thus many efforts have been devoted to study the electrochemical properties of the sulfur electrode for lithium batteries.[2–6] The sulfur, however, does not work successfully as reversible positive electrode materials in lithium batteries using electrolyte solutions, because the electrochemical capacity of the sulfur rapidly fades away on cycling.[2–6] The capacity fading has been attributed to the facts that the reduction of sulfur produces several lithium polysulfides in the batteries and the lithium polysulfides can dissolve into the electrolyte solutions of the batteries.

All-solid-state lithium secondary batteries using inorganic solid electrolytes such as lithium germanium thiophosphate (Thio-LISICON),[7,8] and sulfide glasses in the systems Li_2S–SiS_2,[9–13] Li_2S–P_2S_5,[14,15] and Li_2S–P_2S_3[16] are promising devices with high-safety performance and high-energy density against to conventional lithium ion batteries with electrolyte solutions. The advantages of the all-solid-state batteries are ascribed to nonflammable properties of the inorganic solid electrolytes.

The inorganic solid electrolytes also do not dissolve the lithium polysulfides that are produced during the discharge process of the sulfur electrode. Thus we expect that the elemental sulfur works successively as positive electrode materials of the all-solid-state lithium batteries with the inorganic solid electrolytes.

In this study, we report discharge–charge properties of the sulfur electrode in the all-solid-state lithium battery with the inorganic solid electrolyte and compare the discharge–charge properties of the solid-state battery with those of the conventional lithium battery employing the electrolyte solutions.

For the investigation of the electrochemical properties of sulfur we employed two types of laboratory-scale batteries. One of them was the all-solid-state battery with an inorganic solid electrolyte and the other one was the conventional test battery with an electrolyte solution. For assembling the all-solid-state battery, amorphous (a)-$60Li_2S{\cdot}40SiS_2$ (mol %) powder was employed as the inorganic solid electrolyte. The a-$60Li_2S{\cdot}40SiS_2$ powder was prepared by using a high-energy ball-milling process. The detailed preparation procedure was described elsewhere.[13] The a-$60Li_2S{\cdot}40SiS_2$ powder has shown the high ionic conductivity of $1.8 \times 10^{-4}\,S{\cdot}cm^{-1}$ at 298 K. The negative electrode of the solid-state battery was the ball-milled $Li_{4.4}Ge$ alloy. The detailed preparation procedure was also described elsewhere.[17] The positive electrode was a mixture of sulfur (27 mass%), metallic copper (21.4 mass%), acetylene black powder (1.6 mass%), and the solid electrolyte powder (50 mass%). The mixing procedure of the positive electrode was follows: 1) the sulfur (Wako Chemicals 99%), metallic copper (Wako Chemicals, 99.9%), and acetylene black (Denka) powders were weighed and mixed in an alumina mortar, 2) the mixture was ball-milled for 10 h at room temperature by use of a planetary ball-milling apparatus (Fritsch, P-7), 3) the ball-milled composite and the a-$60Li_2S{\cdot}40SiS_2$ powder were mixed in an agate mortar with a pestle. The all-solid-state battery was assembled by successively pressing the positive electrode mixture, the solid electrolyte (a-$60Li_2S{\cdot}40SiS_2$) powder, and the negative electrode ($Li_{4.4}Ge$ alloy) powder at 300 MPa into a pellet of 10 mm in diameter.

On the other hand, we employed 1M $LiClO_4$-PC solution as the electrolyte solution for the conventional test battery. The counter and reference electrodes of the test battery were metallic lithium. The ball-milled composite of sulfur, copper, and acetylene black powders was also used as the positive electrode materials for the test battery.

The discharge–charge performance of the batteries was tested under constant current densities ($64\,\mu A{\cdot}cm^{-2}$ for the all-solid-state battery and $100\,\mu A{\cdot}cm^{-2}$ for the conventional test battery) at room temperature by use of a battery tester (Hokuto, HJR-110mSM6).

X-ray diffraction (XRD) measurements were performed for the ball-milled composite of sulfur, metallic copper, and acetylene black powders. In the XRD spectrum of the composite, the XRD peaks of the metallic copper have disappeared and the peaks of CuS phase have newly appeared. The results suggest that the metallic copper has reacted with the sulfur during the ball milling and consequently the CuS phase has precipitated in the ball-milled composite.

The XRD peaks of the elemental sulfur have remained in the XRD spectrum of the ball-milled composite. This fact is reasonable, because the mole ratio of the sulfur to copper of the composite is S:Cu = 2.5:1. Assuming that the all of the metallic copper used as raw materials changes into CuS during the milling process, the mole ratio of CuS:S is calculated to be 1:1.5 in the composite electrode.

Figure 1 shows discharge–charge cycling curves of the battery with the electrolyte solution of 1M $LiClO_4$-PC at a constant current density of $100\,\mu A{\cdot}cm^{-2}$. The abscissa of the figure is the specific capacity of the sulfur; the capacity is calculated on the basis of the mass of sulfur that has been used as starting materials.

The first discharge curve shows three plateaus at 2.4, 2.0, and 1.6 V. The total capacity of the first discharge is about 430 mA·h·g^{-1}. After the first cycle, the voltage plateau at 2.4 V disappeares in the discharge curves and the discharge capacity of the cell rapidly fades away on cycling. This result indicates that the positive electrode mixture containing sulfur does not work reversibly in the cell with the electrolyte solution.

After the discharge–charge cycling test, the color of the electrolyte solution turned into yellow. The yellow color was attributed to the soluble polysulfide ions.[18] Thus, the irreversibility of the battery was caused by the polysulfide ions as mentioned above.

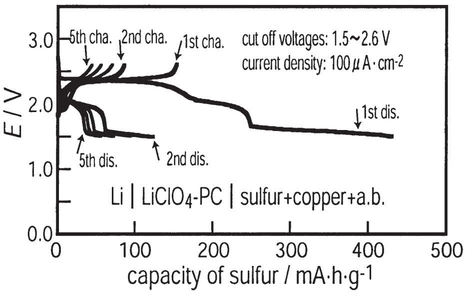

Figure 1. Discharge–charge cycle behavior of the conventional lithium battery with the ball-milled composite of sulfur, copper, and acetylene black powders as positive electrode materials and with the electrolyte solution of 1M $LiClO_4$-PC.

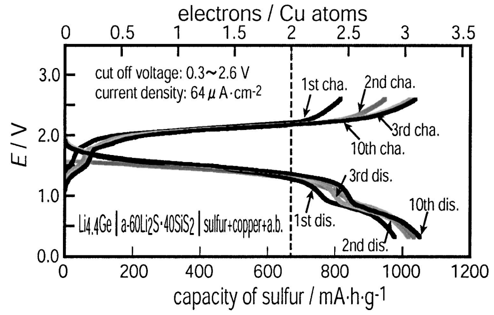

Figure 2. Discharge–charge cycle behavior of the all-solid-state lithium battery with the ball-milled composite of sulfur, copper, and acetylene black powders as positive electrode materials and with the solid electrolyte of a-$60Li_2S{\cdot}40SiS_2$ (mol %).

Figure 2 shows discharge–charge cycle behavior of the all-solid-state battery. The abscissa of the figure is the specific capacity of the sulfur used as starting materials for the ball-milled composite electrode. Two plateaus are observed at 1.5 and 0.7 V in the first discharge curve. The total capacity of the first discharge is about 980 mA·h·g^{-1}. The $Li_{4.4}Ge$ alloy used as the negative electrode materials of the all-solid-state battery shows the electrochemical potential of about 0.6 to 0.3 V against the Li/Li^+ electrode.[17] This fact is one factor causing the voltage differences between the all-solid-state battery and the conventional battery with the electrolyte solution.

In the first charge, two plateaus are also observed at 1.3 and 2.0 V. The total capacity of the first charge is about 810 mA·h·g^{-1}. After the first cycle, the discharge and charge curves show almost the same properties and rechargeable specific capacities are about 1080 mA·h·g^{-1}. The all-solid-state battery shows good discharge–charge reversibility with the large specific capacity.

On the discharge and charge mechanism of the all-solid-state battery, there is a question that only the copper sulfides in the composite electrode work as active materials,[19] not sulfur.

The mole ratio of the reacted electrons to the total copper atoms included in the electrode, e^-/Cu, is additionally plotted in the top abscissa of the figure. When we supposed that the metallic copper was completely converted into the stoichiometric CuS phase by the ball-milling process, the CuS is theoretically able to accept two electrons. The theoretical value is indicated by a broken line in the figure. The discharge and charge capacities of the all-solid-state batteries are beyond the theoretical value. The results suggest that not only the CuS but also the elemental sulfur contributes to the electrochemical reactions of the composite electrode.

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