J Mater Sci (2010) 45:377–381
DOI 10.1007/s10853-009-3948-z

# Characterization of $Li_2S$–$P_2S_5$–Cu composite electrode for all-solid-state lithium secondary batteries

**Akitoshi Hayashi · Ryoji Ohtsubo · Motohiro Nagao · Masahiro Tatsumisago**

Received: 4 May 2009 / Accepted: 3 October 2009 / Published online: 22 October 2009

**Abstract** Electrochemical performance of the $Li_2S$–$P_2S_5$–Cu composite materials was examined in all-solid-state lithium secondary batteries. The $80Li_2S{\cdot}20P_2S_5$ (mol.%) solid electrolyte with the addition of Cu was partially used as an active material with lithium source in all-solid-state cells. The initial discharge capacity of 110 mAh $g^{-1}$ (normalized by the weight of $80Li_2S{\cdot}20P_2S_5$–Cu), which corresponds to 400 mAh $g^{-1}$ (normalized by the weight of $Li_2S$), was obtained in the cell using the $80Li_2S{\cdot}20P_2S_5$–Cu composite electrode with the molar ratio of $Li_2S/Cu = 48/52$. Cycling performance and reaction mechanism of the electrode in the solid-state cell were investigated.

## Introduction

All-solid-state lithium secondary batteries using inorganic materials attract much attention from the viewpoint of safety and reliability. In particular, bulk-type solid-state cells, which are composed of electrode and electrolyte powders, have an advantage of achieving large energy density. Key materials to realize bulk-type lithium batteries are a solid electrolyte with high $Li^+$ ion conductivity and an electrode with high capacity.

We have developed the $Li_2S$–$P_2S_5$ glass–ceramic electrolytes, which showed high conductivity of $10^{-3}$ S $cm^{-1}$ at room temperature and wide electrochemical window of more than 5 V [1, 2]. Bulk-type solid-state In/$LiCoO_2$ cells with the electrolytes exhibited high capacity of 100 mAh $g^{-1}$ for 500 cycles at room temperature [3].

Lithium sulfide ($Li_2S$) is the indispensable component of solid electrolytes. In addition, it is also useful as an active material with high capacity; $Li_2S$ is the final product after discharge process of sulfur electrode with high theoretical capacity (1,672 mAh $g^{-1}$) in Li/S batteries [4–8]. It is difficult to apply $Li_2S$ as well as S to solid-state cells because of their insulative nature. The S and $Li_2S$ particles were thus activated as an active material by adding Cu and consecutive ball-milling [9–11]. All-solid-state Li–In/S–Cu cells with $Li_2S$–$P_2S_5$ solid electrolytes showed excellent cycling performance and retained high capacity of 650 mAh $g^{-1}$ for 20 cycles at room temperature [10]. The cells using $Li_2S$–Cu electrodes also worked as a rechargeable battery with the initial capacity of *ca.* 500 mAh $g^{-1}$ [11]. The $Li_2S$–$P_2S_5$ electrolyte used for solid-state batteries includes a $Li_2S$ component and thus the electrolyte itself has a potential utilization as an active material by adding Cu particles.

Bulk-type solid-state cells are usually assembled using composite electrodes composed of three kinds of powder materials: an active material, a solid electrolyte, and a conductive additive (such as acetylene-black). The design of the composite electrodes is very important to secure favorable solid–solid contacts with continuous conducting paths of lithium ions and electrons [12]. In order to improve energy density of solid-state batteries, it is useful that lithium ion can be electrochemically extracted from not only an active material but also the $Li_2S$–$P_2S_5$ electrolyte in the composite electrode. The Cu-added $Li_2S$–$P_2S_5$ material would play a role as an active material besides an electrolyte with lithium ion conduction path.

In the present study, composite materials were prepared by mixing $Li_2S$–$P_2S_5$ electrolyte and Cu powders. Electrochemical properties of the $Li_2S$–$P_2S_5$–Cu composite

---

A. Hayashi (✉) · R. Ohtsubo · M. Nagao · M. Tatsumisago
Department of Applied Chemistry, Graduate School
of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho,
Naka-ku, Sakai, Osaka 599-8531, Japan
e-mail: hayashi@chem.osakafu-u.ac.jp

material were investigated as a working electrode in all-solid-state cells. The possibility of using the $Li_2S–P_2S_5$ component as an active material in the composite electrode was investigated. Structural change of the electrode during charge–discharge cycles was analyzed by using ex situ X-ray diffraction (XRD) and Raman spectroscopy.

## Experimental

The $80Li_2S·20P_2S_5$ (mol.%) glass–ceramic electrolyte with high conductivity of $10^{-3}$ S $cm^{-1}$ at room temperature was prepared by mechanical milling and heat treatment [1]. The $80Li_2S·20P_2S_5$–Cu composite electrode powder was obtained by grinding in an agate mortar of copper, the $80Li_2S·20P_2S_5$ solid electrolyte, and acetylene-black with the weight ratio of 38/57/5, which is a typical ratio of the composite electrode in bulk-type solid-state cells [3] in the case of replacing copper with an active material; the weight ratio corresponds to the molar ratio of $Li_2S/Cu = 48/52$. The composites at the different compositions of $Li_2S/Cu =$ 75/25, 86/14, and 100/0 were also obtained for comparison. The morphology of the composites was investigated by a scanning electron microscope (SEM; JEOL, JSM-5300) coupled with an energy dispersive X-ray spectrometer (EDX; JEOL, JED-2001).

All-solid-state cells of In/$80Li_2S·20P_2S_5$ electrolyte/$80Li_2S·20P_2S_5$–Cu composite electrode were fabricated. The $80Li_2S·20P_2S_5$–Cu composite powder as a working electrode and the solid electrolyte powder were put together in a polycarbonate tube and then were pressed under 360 MPa to obtain a bilayer pellet. An In foil as a counter electrode was pressed under 120 MPa on the obtained bilayer pellet. After releasing the pressure, the three-layer pellet was sandwiched by two stainless-steel disks as current collectors to form two-electrode cells. The cells were charged and discharged under a constant current density of 64 μA $cm^{-2}$ at 25 °C in an Ar atmosphere using a charge–discharge measuring device (BTS-2004, Nagano Co.). In order to analyze charge–discharge mechanism of the composite electrodes in all-solid-state cells, XRD and Raman measurements of the working electrode after charge–discharge tests were carried out using a XRD diffractometer (M18XHF22-SRA, Mac Science) with CuKα radiation and a Raman spectrometer (RMP-210, JEOL) with green laser (wavelength: 532 nm).

## Results and discussion

Figure 1 shows the SEM image (a) and the EDX mapping images of S (b) and Cu (c) of the $80Li_2S·20P_2S_5$–Cu composite with the molar ratio of $Li_2S/Cu = 48/52$. The composite powders prepared are partially aggregated to form secondary particles with the size of 1–20 μm. Mapping images about S and Cu elements show the presence of the $80Li_2S·20P_2S_5$ electrolyte and Cu particles, respectively, and suggest that the electrolyte and Cu particles are located individually but both particles have a close contact with each other.

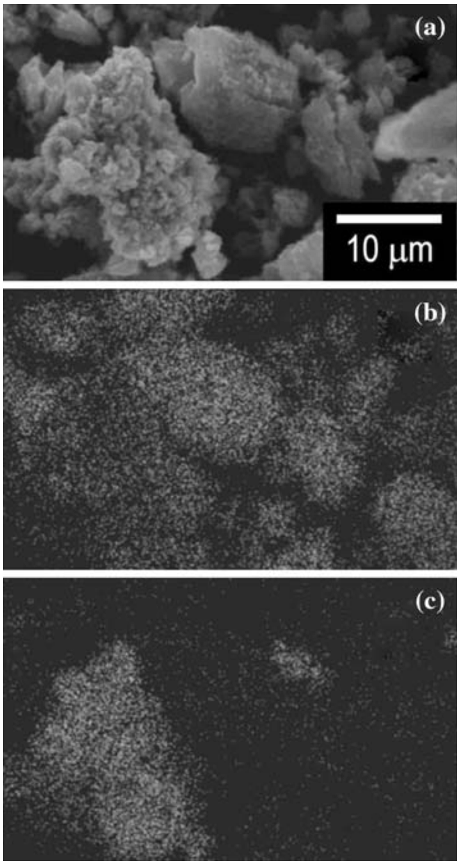

**Fig. 1** SEM image (**a**) and EDX mapping images of S (**b**) and Cu (**c**) of the $80Li_2S·20P_2S_5$–Cu composite with the molar ratio of $Li_2S/Cu = 48/52$

Figure 2 shows the initial charge–discharge curves of the all-solid-state cells In/$80Li_2S·20P_2S_5$ electrolyte/$80Li_2S·20P_2S_5$–Cu at the current density of 64 μA $cm^{-2}$; the molar ratios of $Li_2S/Cu$ in the $80Li_2S·20P_2S_5$–Cu composites are (a) 100/0, (b) 86/14, (c) 75/25, and (d) 48/52. The cell capacity was described as the normalized capacity by the weight of $80Li_2S·20P_2S_5$–Cu. It was difficult for the cell (a) using the $80Li_2S·20P_2S_5$ electrolyte without Cu as a working electrode to be charged and discharged, indicating that the $80Li_2S·20P_2S_5$ electrolyte itself is electrochemically inactive. On the other hand, the cells using the composite electrodes by mixing Cu and $80Li_2S·20P_2S_5$ electrolyte were initially charged and then discharged. It is noteworthy that the $80Li_2S·20P_2S_5$ electrolyte was partially used as an active material by the addition of Cu. The initial charge

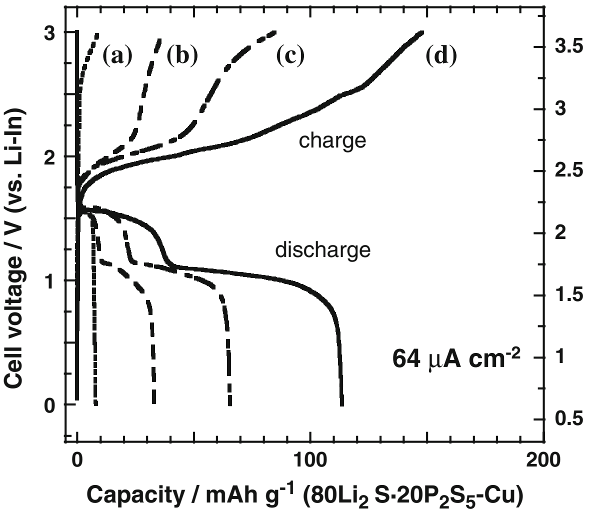

**Fig. 2** Initial charge–discharge curves of the all-solid-state cells In/80$Li_2S$·20$P_2S_5$–Cu at the current density of 64 µA $cm^{-2}$; the molar ratios of $Li_2S$/Cu in the 80$Li_2S$·20$P_2S_5$–Cu composite electrodes are **a** 100/0, **b** 86/14, **c** 75/25, and **d** 48/52

profile showed one plateau, while the discharge profile showed two plateaus. The increase of Cu content in the composites enhanced the charge–discharge capacity of the cells. The composite electrode with $Li_2S$/Cu = 48/52 (d) showed the largest initial capacity; the charge and discharge capacities were *ca.* 150 and 110 mAh $g^{-1}$, respectively.

The charge–discharge mechanism of the 80$Li_2S$·20$P_2S_5$–Cu composite electrodes was examined by ex situ XRD measurements. Figure 3 shows the XRD patterns of the 80$Li_2S$·20$P_2S_5$–Cu composite electrode with $Li_2S$/Cu = 48/52 before (a) and after the charge to 3.0 V (b), after the discharge from 3.0 to 1.2 V (c), and after the discharge from 3.0 to 0 V (d). Before charge (a), the XRD peaks attributable to Cu and the 80$Li_2S$·20$P_2S_5$ glass–ceramic electrolyte, consisting of $Li_2S$ and thio-LISICON analog [1] crystals, were observed. The intensity of the peaks due to Cu decreased and the peaks due to $Li_2S$ in the electrolyte disappeared after charge to 3.0 V (b). The peaks due to $Cu_{1.8}S$ newly appeared at this stage. After discharge from 3.0 to 1.2 V ((c), the endpoint of the first plateau), the XRD pattern was almost the same as that before discharge (b). The peaks due to $Cu_{1.8}S$ disappeared and then the peaks due to $Li_2S$ and $Cu_{1.96}S$ appeared after discharge to 0 V ((d), after the second plateau).

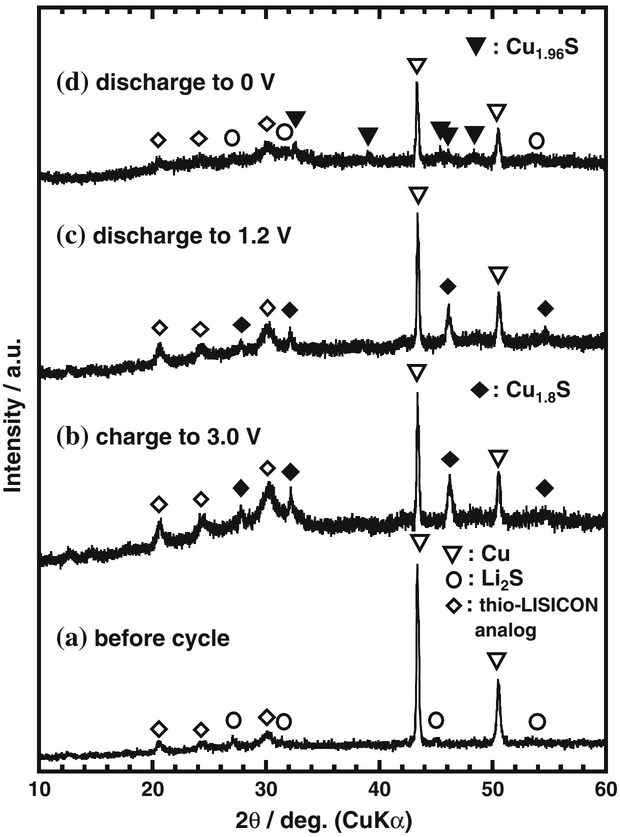

**Fig. 3** XRD patterns of the 80$Li_2S$·20$P_2S_5$–Cu composite electrode with $Li_2S$/Cu = 48/52 before (**a**) and after the charge to 3.0 V (**b**), after the discharge from 3.0 to 1.2 V (**c**), and after the discharge from 3.0 to 0 V (**d**)

The XRD results suggest the following reaction mechanism of the 80$Li_2S$·20$P_2S_5$–Cu composite electrode. At the initial charge process, $Li_xCu_yS$ domains would be formed by reaction between Cu and $Li_2S$ and then lithium ions are deintercalated from the $Li_xCu_yS$ domains to finally form $Cu_{1.8}S$. Lithium insertion to $Cu_{1.8}S$ to form $Li_xCu_{1.8}S$ is a possible process at the first discharge plateau. A similar discharge mechanism is reported in a cell using the CuS electrode [13], in which the first discharge plateau corresponds to the formation of $Li_xCuS$ by lithium insertion to CuS; the XRD patterns of $Li_xCuS$ are almost the same as those of CuS. Further lithium insertion to $Li_xCu_{1.8}S$ produced $Cu_{1.96}S$ and $Li_2S$ at the end of the second discharge plateau.

Copper sulfide $Cu_{1.8}S$ was formed during the initial charge process and then $Cu_{1.8}S$ worked as active materials during a consecutive discharge process. The increase of the Cu content in the 80$Li_2S$·20$P_2S_5$–Cu composite electrode would lead to the formation of large $Cu_{1.8}S$ active domains and thus the increase of initial cell capacity as shown in Fig. 2. The thio-LISICON analog ($Li_{3+5z}P_{1-z}S_4$) in the solid electrolyte was possibly used in electrochemical reaction. However, structural change of the thio-LISICON analog was not clearly observed by ex situ XRD measurements as shown in Fig. 3; structural analyses by several spectroscopic techniques are needed to clarify the role of thio-LISICON analog in electrochemical reaction.

Figure 4 shows cycle performance of the all-solid-state cells In/80$Li_2S$·20$P_2S_5$ electrolyte/80$Li_2S$·20$P_2S_5$–Cu with molar ratio of $Li_2S$/Cu = 48/52 and 75/25. A constant current density of 64 µA $cm^{-2}$ was used. Although larger initial capacity was obtained in the cell using the

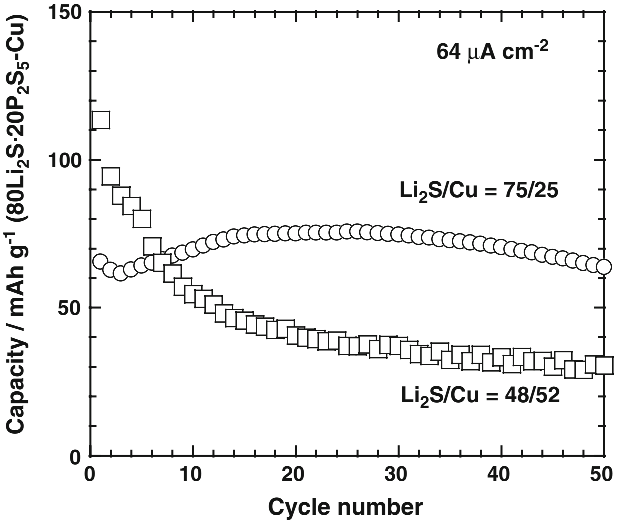

**Fig. 4** Cycle performance of the all-solid-state cells In/$80Li_2S \cdot 20P_2S_5$–Cu with molar ratio of $Li_2S$/Cu = 48/52 and 75/25. A constant current density of 64 μA $cm^{-2}$ was used

$80Li_2S \cdot 20P_2S_5$–Cu electrode with $Li_2S$/Cu = 48/52 as shown in Fig. 2, the cell with $Li_2S$/Cu = 75/25 exhibited better cycle performance and retained the capacity of about 60 mAh $g^{-1}$ after 50 cycles. The capacity of the cell with $Li_2S$/Cu = 48/52 drastically decreased during charge–discharge cycling, and the cell showed about 30 mAh $g^{-1}$ after 50 cycles.

To elucidate a potential reason of capacity fading, structure of the composite electrode before and after charge–discharge cycles was analyzed by XRD and Raman techniques. Figure 5 shows XRD patterns (a) and Raman spectra (b) of the $80Li_2S \cdot 20P_2S_5$–Cu composite electrode with $Li_2S$/Cu = 48/52 before cycling and after the 1st and 50th cycles. The XRD peaks due to $Cu_{1.96}S$ were observed after the 1st cycle (the 1st discharge), while the peaks due to $Cu_{1.8}S$, which was the product after the 1st charge as shown in Fig. 3, were observed after the 50th cycle (the 50th discharge). The intensity of the peaks due to Cu was considerably decreased and the peaks due to $Li_2S$ disappeared after the 50th cycle. The Raman peak at 420 $cm^{-1}$, which is attributable to $PS_4^{3-}$ ions in the thio-LISICON analog (in the electrolyte) [14], was observed in the Raman spectra of the composite electrode before and after the 1st cycle. After the 50th cycle, the peak at 470 $cm^{-1}$ was newly observed in addition to the $PS_4^{3-}$ peak. The peak at 470 $cm^{-1}$ is attributable to several copper sulfides $Cu_xS$ ($x$ = 1.0, 1.8, and 2.0) [15, 16]. Structural analyses suggest that gradual reaction of $Li_2S$ in the electrolyte and Cu during charge–discharge for 50 cycles formed large copper sulfide domains, which play a role in preventing lithium ion conduction path supplied by the electrolyte. Lack of lithium ion conduction in the composite electrode is a possible reason of capacity fading of the electrode with $Li_2S$/Cu = 48/52 as shown in Fig. 4. On the other hand, the electrode with $Li_2S$/Cu = 75/25 exhibited better cycling performance in an all-solid-state cell. Figure 6 shows Raman spectra of the $80Li_2S \cdot 20P_2S_5$–Cu composite electrodes with $Li_2S$/Cu = 75/25 and 48/52 after charge–discharge for 50 cycles. In the cell using the electrode with $Li_2S$/Cu = 75/25, the Raman peak due to copper sulfides at 470 $cm^{-1}$ was also observed, but the peak intensity was considerably lower than that in the cell with $Li_2S$/Cu = 48/52. The decrease of Cu content in the electrode is useful for preventing excess formation of copper sulfide domains

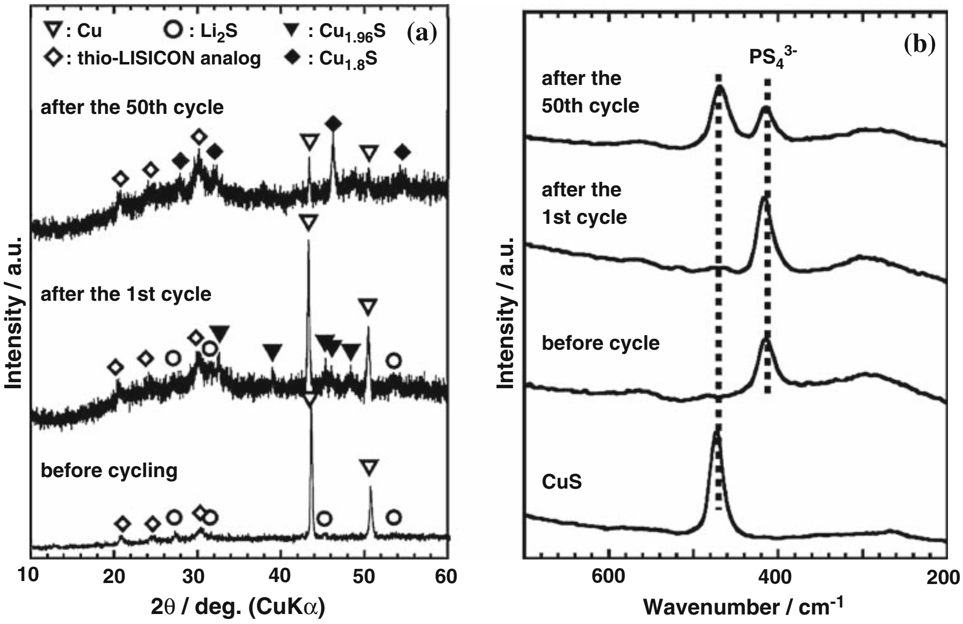

**Fig. 5** XRD patterns (**a**) and Raman spectra (**b**) of the $80Li_2S \cdot 20P_2S_5$–Cu composite electrode with $Li_2S$/Cu = 48/52 before cycling and after the 1st and 50th cycles

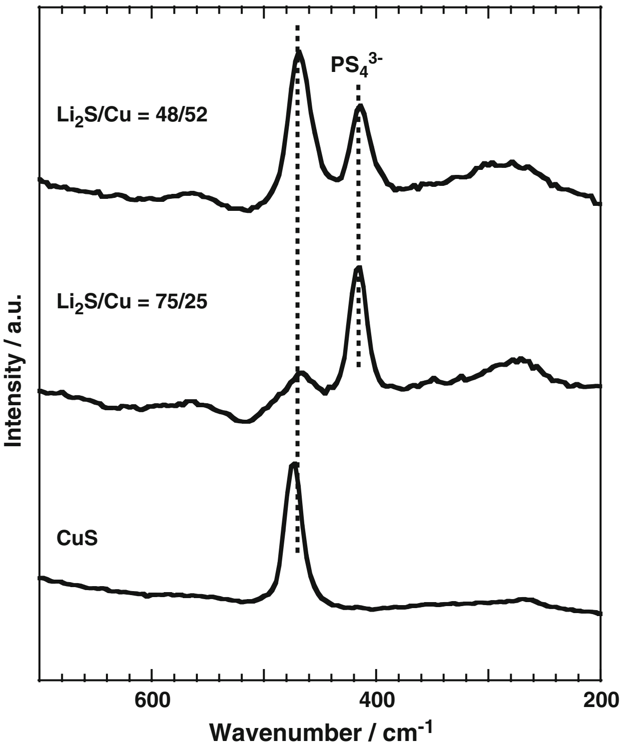

**Fig. 6** Raman spectra of the $80Li_2S{\cdot}20P_2S_5$–Cu composite electrodes with $Li_2S/Cu = 75/25$ and 48/52 after charge–discharge for 50 cycles. The spectrum of CuS is also shown for comparison

during cycling and it would bring about good cyclability of the cell using the electrode with $Li_2S/Cu = 75/25$.

## Conclusions

The $80Li_2S{\cdot}20P_2S_5$ solid electrolyte with the addition of Cu was used as an active material with lithium source in all-solid-state cells. Of course, the electrolyte itself was electrochemically inactive and the cell was not charged and discharged. It was revealed that the $80Li_2S{\cdot}20P_2S_5$ electrolyte functioned as an active material by the addition of Cu. The increase of the Cu content in the composite electrode $80Li_2S{\cdot}20P_2S_5$–Cu enhanced initial charge–discharge capacity of the cells. The initial discharge capacity of 110 mAh $g^{-1}$ (normalized by the weight of $80Li_2S{\cdot}20P_2S_5$–Cu), which corresponds to 400 mAh $g^{-1}$ (normalized by the weight of $Li_2S$), was obtained in the cell using the composite electrode with the molar ratio of $Li_2S/Cu = 48/52$. The formation of $Li_xCu_yS$ active domains on the initial charge process is responsible for the cell capacity. The composite electrode with the molar ratio of $Li_2S/Cu = 75/25$ exhibited better cycle performance and retained the capacity of 60 mAh $g^{-1}$ of $80Li_2S{\cdot}20P_2S_5$–Cu, which corresponds to 170 mAh $g^{-1}$ of $Li_2S$. A composite electrode including not only active material powders but also solid electrolyte powders is indispensable for operating bulk-type solid-state batteries. Partial use of the $Li_2S$–$P_2S_5$ electrolytes as an active material by adding Cu is effective in increasing energy density of the batteries.

**Acknowledgements** This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan, and also supported by the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

## References

1. Hayashi A, Hama S, Minami T, Tatsumisago M (2003) Electrochem Commun 5:111
2. Hayashi A, Hama S, Mizuno F, Tadanaga K, Minami T, Tatsumisago M (2004) Solid State Ion 175:683
3. Minami T, Hayashi A, Tatsumisago M (2006) Solid State Ion 177:2715
4. Yamin H, Gorenshtein A, Penciner J, Sternberg Y, Peled E (1988) J Electrochem Soc 135:1045
5. Marmorstein D, Yu TH, Striebel KA, McLarnon FR, Hou J, Cairns EJ (2000) J Power Sources 89:219
6. Akridge JR, Mikhaylik YV, White N (2004) Solid State Ion 175:243
7. Ryu HS, Ahn HJ, Kim KW, Ahn JH, Lee JY (2006) J Power Sources 153:360
8. He X, Pu W, Ren J, Wang L, Wang J, Jiang C, Wan C (2007) Electrochim Acta 52:7372
9. Machida N, Kobayashi K, Nishikawa Y, Shigematsu T (2004) Solid State Ion 175:247
10. Hayashi A, Ohtomo T, Mizuno F, Tadanaga K, Tatsumisago M (2004) Electrochim Acta 50:893
11. Hayashi A, Ohtsubo R, Ohtomo T, Mizuno F, Tatsumisago M (2008) J Power Sources 183:422
12. Mizuno F, Hayashi A, Tadanaga K, Tatsumisago M (2006) Solid State Ion 177:2731
13. Chung JS, Sohn HJ (2002) J Power Sources 108:226
14. Tachez M, Malugani JP, Mercier R, Robert G (1984) Solid State Ion 14:181
15. Minceva-Sukarova B, Najdoski M, Grozdanov I, Chunnilall CJ (1997) J Mol Struct 410–411:267
16. Liu Y, Cao J, Wang Y, Zeng J, Qian Y (2002) Inorg Chem Commun 5:407