



Short communication

All-solid-state rechargeable lithium batteries with Li_2S as a positive electrode material[☆]Akitoshi Hayashi^{*}, Ryoji Ohtsubo, Takamasa Ohtomo, Fuminori Mizuno, Masahiro Tatsumisago

Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan

ARTICLE INFO

Article history:

Available online 18 May 2008

Keywords:

All-solid-state battery

Lithium battery

Solid electrolyte

Positive electrode

Li/S battery

Mechanical milling

ABSTRACT

The Li_2S –Cu composite electrode materials were prepared by mechanical milling and applied to all-solid-state lithium cells using the Li_2S – P_2S_5 glass–ceramic electrolyte. The addition of Cu and the mechanical activation improved the electrochemical performance of Li_2S in all-solid-state cells. The In/ Li_2S –Cu cells were charged and then discharged at room temperature, suggesting that Li_2S was utilized as a lithium source. The cells exhibited high discharge capacity of about 490 mAh g^{-1} at the 1st cycle. The SEM and EDX analyses suggested that the amorphous Li_xCuS domain was partially formed by milling, and the domain played an important role in the improvement of capacity. The electrochemical reaction mechanism of the Li_2S –Cu composites was discussed on the basis of the mechanism of the S–Cu composite electrode.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

All-solid-state rechargeable lithium batteries using inorganic solid electrolytes attract much attention because these batteries possess high safety and reliability without leakage and inflammability of electrolytes [1]. Superior cyclability is another feature of solid-state batteries. Thin film lithium batteries using inorganic glassy electrolytes such as the Lipon (lithium phosphorus oxynitride) glass were reported to show excellent long-cycling performances for over 50,000 cycles at room temperature [2]. On the other hand, bulk-type batteries have been developed by using sulfide solid electrolytes with high conductivity such as the Li_2S – SiS_2 – Li_3PO_4 glasses [3,4], the Li_2S – P_2S_5 glass–ceramics [5], and the Li_2S – P_2S_5 – GeS_2 thio-LISICON crystals [6]. In particular, the all-solid-state cell of In/ LiCoO_2 with the 80 Li_2S –20 P_2S_5 (mol%) glass–ceramic electrolyte retained high capacity of 100 mAh g^{-1} for 500 cycles at room temperature [7].

The development of new positive electrode materials with high capacity is indispensable for improving rechargeable lithium batteries. Elemental sulfur is one of the promising candidates because of its advantages of a large theoretical capacity of 1672 mAh g^{-1} , low cost, and environmental friendliness. One of the serious problems on Li/S batteries with conventional liquid electrolyte is a capac-

ity fading during cycling due to the dissolution of polysulfides into liquid electrolytes [8–11].

The replacement of liquid electrolyte with inorganic solid electrolyte overcomes the drawback of the Li/S cells mentioned above. The all-solid-state Li/S cells were assembled by using the Li_2S – SiS_2 glasses [12,13] and the Li_2S – P_2S_5 glass–ceramics [14,15]. Unfortunately, the cells with sulfur itself as an active material were not charged and discharged because of its insulative nature. The S–Cu composite materials were then prepared by mechanical milling of the mixture of sulfur and copper powders. The all-solid-state Li–In/S–Cu cells worked as a rechargeable battery at room temperature and exhibited high capacity of 650 mAh g^{-1} for 20 cycles [14,15]. The mechanochemically activated S–Cu composite is a promising positive electrode with high capacity in all-solid-state cells. The reaction products after lithium insertion to the S–Cu composite were Li_2S and Cu. The utilization of Li_2S as a positive electrode material is then attractive from the viewpoint of the diversification of selecting negative electrodes without lithium sources. Obrovac and Dahn have already reported the possibility of the Li_2S –Fe composite as an active material for lithium-ion batteries [16]. The combination of Li_2S –metal would be applicable to all-solid-state batteries.

In the present study, the Li_2S –Cu composite materials were prepared by mechanical milling of the mixture of crystalline Li_2S and Cu powders. The crystal phases and morphology of the obtained samples were investigated. The composites were applied as a positive electrode to all-solid-state cells, and the electrochemical performance of the In/ Li_2S –Cu cells was examined. The

[☆] Selected papers presented at the IMLB 2006—International Meeting on Lithium Batteries.

^{*} Corresponding author.

E-mail address: hayashi@chem.osakafu-u.ac.jp (A. Hayashi).

charge–discharge mechanism of the Li_2S –Cu composite electrode will be discussed.

2. Experimental

Reagent-grade Li_2S (Idemitsu Kosan Co., >99.9%) and copper (Wako Chem., 99.9%) crystalline powders were used as starting materials for sample preparation. The mechanochemical treatment was carried out for the batches (1 g) of the mixture of Li_2S and Cu with the molar ratio of $\text{Li}_2\text{S}/\text{Cu}=3$ in an alumina pot (volume of 45 mL) with ten alumina balls (10 mm in diameter) using a high-energy planetary ball mill apparatus (Fritsch Pulverisette 7). The rotating speed was fixed to 370 rpm. The molar ratio was selected because the S–Cu positive electrode with the ratio of S/Cu = 3 exhibited the highest capacity and cyclability in all-solid-state cells [15]. All the processes were performed in a dry Ar-filled glove box ($[\text{H}_2\text{O}] < 1$ ppm). X-ray diffraction (XRD) measurements ($\text{Cu K}\alpha$) were performed using a diffractometer (M18XHF²²-SRA, MAC Science) to identify crystalline phases in the prepared Li_2S –Cu materials. The morphology of the materials was investigated by a scanning electron microscope (SEM; JEOL, JSM-5300) coupled with an energy dispersive X-ray spectrometer (EDX; JEOL, JED-2001).

The $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$ (mol%) glass–ceramic solid electrolytes were prepared by mechanical milling and subsequent heat treatment [17]. The mixture of reagent-grade Li_2S (Furuuchi Chem., 99.9%) and P_2S_5 (Aldrich, 99%) crystalline powders was put into an Al_2O_3 pot with Al_2O_3 balls, and then was mechanically milled for 20 h under a rotating speed of 370 rpm by using the planetary ball mill apparatus. The obtained glassy powder was heated at 230°C to yield the glass–ceramics with high conductivity of 10^{-3} S cm^{-1} at room temperature.

Laboratory-scale solid-state cells were constructed as follows. The composite positive electrode powder was obtained by mixing of the Li_2S –Cu materials prepared above, the glass–ceramic, and acetylene-black with the weight ratio of 38:57:5. The composite powder (10 mg) as a positive electrode and the glass–ceramic powder (80 mg) as a solid electrolyte were placed in a polycarbonate tube ($\phi = 10$ mm) and pressed together under 3700 kg cm^{-2} , and then an Indium foil as a negative electrode was pressed under 1200 kg cm^{-2} on the pellet. After releasing the pressure, the obtained pellet was sandwiched by two stainless-steel rods as current collectors. The cells were assembled with an excess amount of negative electrode to positive electrode; the molar ratio of negative electrode/positive electrode was about 3. The cells were charged and discharged at room temperature in an Ar atmosphere using a charge–discharge measuring device (BTS-2004, Nagano). The constant current density of $64\mu\text{A cm}^{-2}$ was used for the measurements.

3. Results and discussion

Fig. 1 shows the XRD patterns of powder mixtures of Li_2S and Cu (the molar ratio of $\text{Li}_2\text{S}/\text{Cu}=3$) with different milling periods. The numbers in this figure denote the milling time. Diffraction peaks due to the crystals of Li_2S and Cu are observed in the powder mixture without mechanical milling (0 h). The intensity of the peaks becomes weak with increasing the milling time. The broad peaks due to the starting materials still remain even after milling for 100 h. The XRD results suggest that partial amorphization and/or pulverization of the Li_2S –Cu mixture occur and new crystalline materials are not formed during mechanical activation.

The morphology and elemental mapping (S and Cu) of the mixtures were investigated by SEM and EDX. Fig. 2 shows the

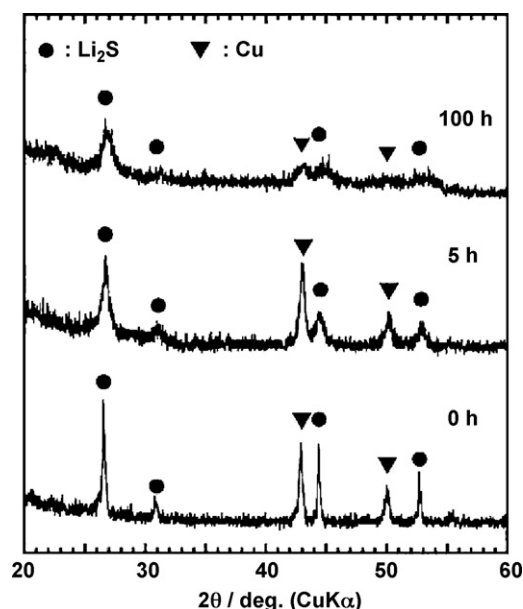


Fig. 1. XRD patterns of powder mixtures of Li_2S and Cu (the molar ratio of $\text{Li}_2\text{S}/\text{Cu}=3$) with different milling periods.

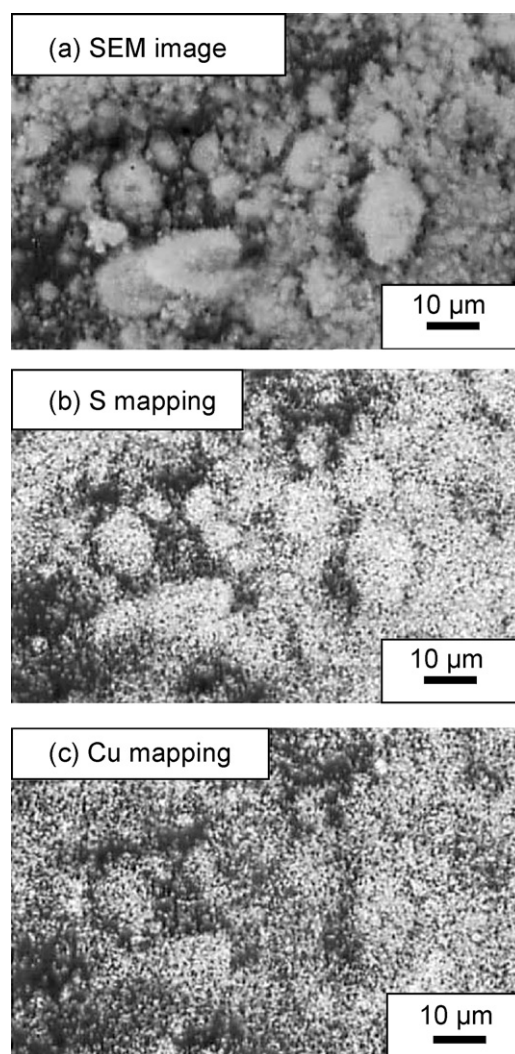


Fig. 2. SEM image (a) and EDX mapping of S (b) and Cu (c) of the Li_2S –Cu composite prepared by milling for 5 h.

SEM image (a) and the EDX mapping of S (b) and Cu (c) of the Li_2S -Cu mixtures prepared by milling for 5 h. The size of the primary particles obtained after milling is below a few μm , although the aggregation of the primary particles is partially observed. The sizes of starting materials were 30–50 μm for the Li_2S powder and 10–20 μm for the Cu powder, suggesting that the mixture was pulverized during milling for 5 h. Further aggregation of the primary particles was observed, but the size of the primary particles was not largely changed with increasing the milling time up to 100 h; amorphization of the Li_2S -Cu materials would be a dominant factor for the broadening of the XRD peaks as shown in Fig. 1. EDX mapping indicates that both signals due to S and Cu are detected from the areas where the particles are placed. It is revealed that the Li_2S and Cu particles are not present separately and both particles are attached together. Because the EDX analysis is sensitive to the surface of the samples, a Li_2S -Cu amorphous product is possibly present at the surface of the particles.

Because of insulative nature of Li_2S , it was difficult for the cell with Li_2S itself as an active material to work as lithium rechargeable batteries even at the low current density of $12.8 \mu\text{A cm}^{-2}$. The addition of Cu to Li_2S improved the electrochemical performance of all-solid-state cells. Fig. 3 shows the first charge-discharge curves of all-solid-state cells of $\text{In}/80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$ glass-ceramic/ Li_2S -Cu. The Li_2S -Cu composites with the molar ratio of $\text{Li}_2\text{S}/\text{Cu} = 3$ prepared by milling for 0, 5, and 100 h were used for active materials. The measurements were carried out at the current density of $64 \mu\text{A cm}^{-2}$ at 25°C . The cell with the as-mixed Li_2S -Cu (0 h) as a positive electrode is charged and then discharged, suggesting that Li_2S can be utilized as a lithium source in all-solid-state rechargeable batteries. The cell shows the discharge capacity of 120 mAh g^{-1} at the 1st cycle, although an irreversible capacity of 30 mAh g^{-1} is observed. An enhancement of the cell performance is achieved by milling for the Li_2S -Cu mixture. The cell with the Li_2S -Cu composite prepared by milling for 5 h exhibits almost fivefold larger reversible capacity than the cell with the as-mixed one. The capacity of the cell with the Li_2S -Cu composite milled for 100 h is lower than that milled for 5 h. The decrease in capacity with increasing milling time would relate to the degree of aggregation of the Li_2S -Cu composite particles; electrochemically inactive domain is increased as the composite particles become more largely aggregated.

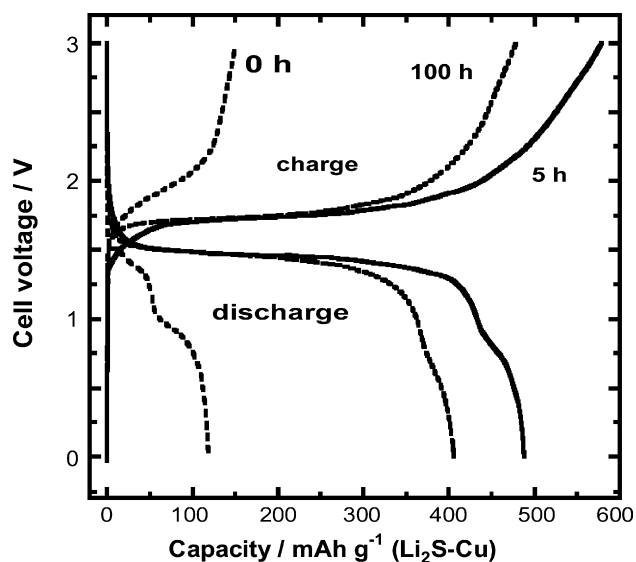


Fig. 3. Charge-discharge curves of all-solid-state cells of $\text{In}/80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$ glass-ceramic/ Li_2S -Cu at the 1st cycle.

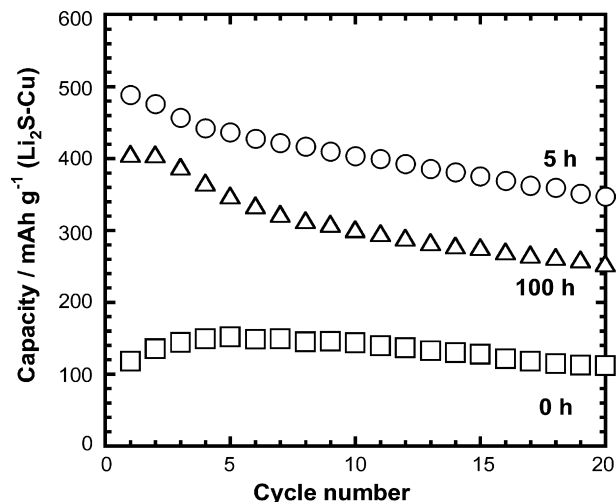


Fig. 4. Cycling performance of all-solid-state cells of $\text{In}/80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$ glass-ceramic/ Li_2S -Cu.

Fig. 4 shows cycling performance of the all-solid-state cells using the Li_2S -Cu composites prepared by milling for 0, 5, and 100 h. The discharge capacities gradually decrease with cycling in the cells with the milled Li_2S -Cu composites, and the capacity of the cell with the composite milled for 5 h is about 350 mAh g^{-1} at the 20th cycle. On the other hand, the capacity initially increases and then decreases with increasing cycle number for the cell with as-mixed Li_2S -Cu (0 h), although the capacity is relatively lower than that of the milled composites.

In order to discuss the charge-discharge mechanism of the Li_2S -Cu electrode materials, the charge-discharge curves of the Li_2S -Cu composites were compared to those of the S-Cu composites [14]. Fig. 5 shows the charge-discharge curves of the cells of $\text{In}/\text{Li}_2\text{S}$ -Cu and $\text{Li-In}/\text{S-Cu}$. The S-Cu composite was prepared by milling of the mixture of S and Cu (the molar ratio of $\text{S}/\text{Cu} = 3$) for 15 min, and the crystalline CuS was partially formed in addition to the remaining S after milling. The cell with Li_2S -Cu milled for 5 h shows only one plateau at both the charge and discharge.

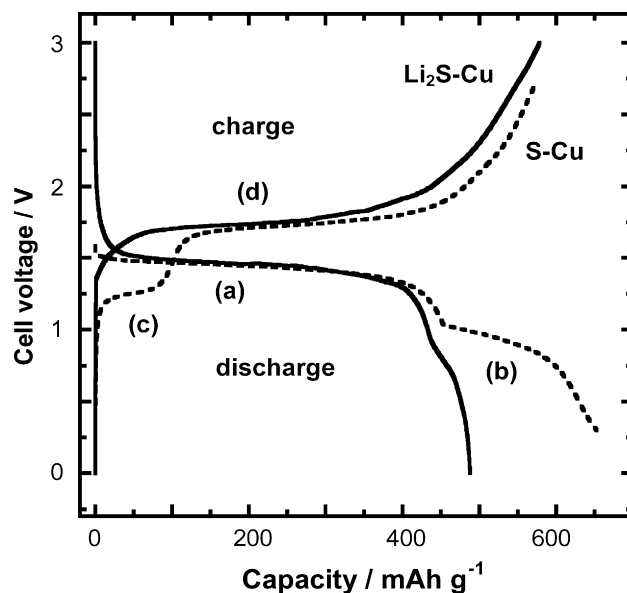
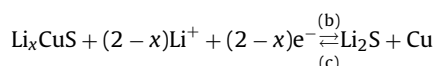
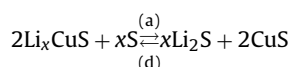
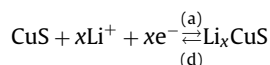


Fig. 5. Charge-discharge curves of the cells of $\text{In}/\text{Li}_2\text{S}$ -Cu and $\text{Li-In}/\text{S-Cu}$ [14] at the 1st cycle.

charge processes, while the cell with S–Cu shows two plateaux. The marks from (a) to (d) on the curves denote the respective plateaux.

It is found that the potential of the charge plateau (d) at 1.8 V of the cell with Li₂S–Cu almost corresponds to one of the two charge plateaux of the cell with S–Cu; the first charge plateau (c) at 1.2 V observed in the S–Cu cell is not found in the Li₂S–Cu cell. On the discharge process, the potential plateau (a) at 1.4 V of the cell with Li₂S–Cu corresponds to one of the two discharge plateaux of the cell with S–Cu.

The charge–discharge mechanism of the S–Cu electrodes was proposed [13–15] and the electrochemical reactions are as follows:



The electrochemical reaction of the cell with Li₂S–Cu would be the same as the reactions (a) and (d) of the cell with S–Cu. Because the former cell was firstly charged and then discharged, the reaction (d) should occur on the first charge process. The reaction (d) needs the compounds such as Li_xCuS as the starting material. The Li_xCuS amorphous moiety, which was not detected from the XRD measurement, would be present in the Li₂S–Cu composites; the SEM and EDX results as shown in Fig. 2 support this speculation. The cells using the Li₂S–Cu milled composite exhibited much higher capacity than the cell with as-mixed powder as shown in Fig. 3. The improvement of the cell performance would be due to the formation of electrochemically active Li_xCuS domains during milling process.

Fig. 6 shows ex situ XRD patterns of the Li₂S–Cu electrode materials (milled for 5 h) after the charge–discharge cycles. In order to prevent the overlap of the peaks due to the Li₂S–P₂S₅ glass–ceramic electrolyte, the Li₂S–SiS₂–Li₄SiO₄ glass [4] was used as a solid electrolyte for this experiment. We confirmed that the difference of solid electrolytes did not affect the charge–discharge profiles. The peaks due to silicon powder as a standard overlap all the XRD patterns. After the 1st charge process, the peaks due to Cu completely disappear and the intensity of the peaks due to Li₂S becomes weak. The new broad peaks, which are attributable to CuS [18], appear. The

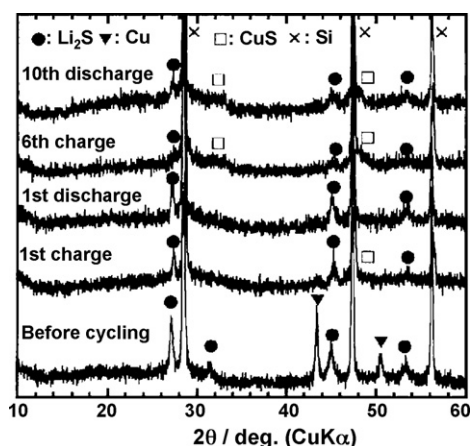


Fig. 6. XRD patterns of the Li₂S–Cu electrode materials (milled for 5 h) after the charge–discharge cycles.

pattern after the 1st discharge process is almost the same as that after the 1st charge, and the peak due to CuS is not observed. The broad peaks due to Li₂S still remain and the CuS peaks are observed after the 6th charge process. The pattern after the 10th discharge process is very similar to that after the 6th charge process.

As shown in Fig. 5, the plateau (c) due to the electrochemical reaction between Li₂S and Cu was not observed in the charge process for the Li₂S–Cu composite. It is, however, revealed from the XRD measurement that the Cu crystal vanished after the 1st charge process. We presume that the chemical reaction between Cu and Li₂S (not electrochemical reaction (c)) partially occurs during charging, and the produced Li_xCuS would also be used as active materials. The XRD peaks due to CuS were not clearly observed after the 1st charge process, and then the electrochemically formed CuS would be present as an amorphous state and/or fine particles. The active sites of Li_xCuS which can contribute to the charge process seem to be utilized as active domain on the consecutive discharge process, and the further reaction (b) (the decomposition of Li_xCuS) would be difficult to proceed.

The capacity fading of the cells with Li₂S–Cu composites as shown in Fig. 4 is discussed from the XRD results. The CuS domain was detected even after the 10th discharge process, suggesting that electrochemically inactive CuS domain is formed during charge–discharge cycles. The contact loss in the composite electrodes, which may occur by volume change during charge–discharge cycles, is one of the reasons for the formation of those inactive sites. In the case of the cell using as-mixed Li₂S–Cu powder, the capacity increased and then decreased as a function of cycle number. The two plateaux observed at the 1st discharge as shown in Fig. 3 became one plateau at 1.4 V. This is because that the electrochemically active domain such as Li_xCuS gradually formed during lithiation–delithiation at the initial cycles, and then the similar capacity fading mentioned above would occur.

4. Conclusions

The composite electrode materials were prepared by mechanical milling for the mixture Li₂S and Cu. It was revealed that the addition of Cu and the mechanical activation improved the electrochemical performance of Li₂S in all-solid-state cells. The all-solid-state cells of In/Li₂S–Cu were assembled by using the Li₂S–P₂S₅ glass–ceramic electrolyte. The cells with the Li₂S–Cu milled composite as a positive electrode were charged and then discharged, suggesting that Li₂S was utilized as a lithium source in all-solid-state rechargeable batteries. The cells exhibited high discharge capacity of about 490 mAh g^{−1} at the 1st cycle. The SEM and EDX analyses suggested that the amorphous Li_xCuS domain was partially formed by milling, and the domain played an important role in the improvement of capacity. The capacity gradually decreased during charge–discharge cycles and the discharge capacity was about 350 mAh g^{−1} at the 20th cycle. The electrochemical reaction mechanism of the Li₂S–Cu composites was discussed on the basis of the mechanism of the S–Cu composite electrode. The mechanochemically activated Li₂S–Cu composite material is a promising positive electrode with high capacity in all-solid-state cells, and possesses an excellent feature of combining with negative electrode materials without lithium sources.

Acknowledgements

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

References

- [1] T. Minami, M. Tatsumisago, in: T. Minami (Ed.), *Solid State Ionics for Batteries*, Springer-Verlag, Tokyo, 2005, p. 1.
- [2] J.B. Bates, *Electron. Eng.* 69 (1997) 63.
- [3] K. Takada, N. Aotani, K. Iwamoto, S. Kondo, *Solid State Ionics* 86–88 (1996) 877.
- [4] A. Hayashi, R. Komiya, M. Tatsumisago, T. Minami, *Solid State Ionics* 152–153 (2002) 285.
- [5] F. Mizuno, A. Hayashi, K. Tadanaga, T. Minami, M. Tatsumisago, *Chem. Lett.* (2002) 1244.
- [6] R. Kanno, M. Murayama, J. *Electrochem. Soc.* 148 (2001) A742.
- [7] T. Minami, A. Hayashi, M. Tatsumisago, *Solid State Ionics* 177 (2006) 2715.
- [8] H. Yamin, A. Gorenshtein, J. Penciner, Y. Sternberg, E. Peled, *J. Electrochem. Soc.* 135 (1988) 1045.
- [9] D. Marmorstein, T.H. Yu, K.A. Striebel, F.R. McLarnon, J. Hou, E.J. Cairns, *J. Power Sources* 89 (2000) 219.
- [10] J. Shim, K.A. Striebel, E.J. Cairns, *J. Electrochem. Soc.* 149 (2002) A1321.
- [11] S.E. Cheon, K.S. Ko, J.H. Cho, S.W. Kim, E.Y. Chin, H.T. Kim, *J. Electrochem. Soc.* 150 (2003) A796.
- [12] N. Machida, T. Shigematsu, *Chem. Lett.* 33 (2004) 376.
- [13] N. Machida, K. Kobayashi, Y. Nishikawa, T. Shigematsu, *Solid State Ionics* 175 (2004) 247.
- [14] A. Hayashi, T. Ohtomo, F. Mizuno, K. Tadanaga, M. Tatsumisago, *Electrochem. Commun.* 5 (2003) 701.
- [15] A. Hayashi, T. Ohtomo, F. Mizuno, K. Tadanaga, M. Tatsumisago, *Electrochim. Acta* 50 (2004) 893.
- [16] M.N. Obrovac, J.R. Dahn, *J. Electrochem. Soc.* 5 (2002) A70.
- [17] A. Hayashi, S. Hama, T. Minami, M. Tatsumisago, *Electrochem. Commun.* 5 (2003) 111.
- [18] J.S. Chung, H.J. Sohn, *J. Power Sources* 108 (2002) 226.