



Short communication

## All solid-state sheet battery using lithium inorganic solid electrolyte, thio-LISICON

Taro Inada<sup>a,b</sup>, Takeshi Kobayashi<sup>a,c</sup>, Noriyuki Sonoyama<sup>a</sup>, Atsuo Yamada<sup>a</sup>, Shigeo Kondo<sup>d</sup>, Miki Nagao<sup>a</sup>, Ryoji Kanno<sup>a,\*</sup>

<sup>a</sup> Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, Nagatsuta, Midori, Yokohama, 226-8502, Japan

<sup>b</sup> Research Center, Denki Kagaku Kogyo K.K., Asahi-machi, Machida, Tokyo, 194-8560, Japan

<sup>c</sup> Materials Science Research Laboratory, Central Research Institute of Electric Power Industry (CRIEPI), 2-11-1, Iwado-kita, Komae, Tokyo, 201-8511, Japan

<sup>d</sup> Department of Chemistry for Materials, Faculty of Engineering, Mie University, 1577 Kurimamachiya-cho, Tsu 514-8507, Japan

### ARTICLE INFO

#### Article history:

Received 12 March 2009

Received in revised form 11 May 2009

Accepted 16 June 2009

Available online 9 July 2009

#### Keywords:

All solid-state battery

Thio-LISICON

Laminate type

### ABSTRACT

All solid-state sheet lithium battery was developed using inorganic solid electrolyte, thio-LISICON ( $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ ), Li–Al anode, and  $\text{Mo}_6\text{S}_8$  cathode materials, and the sheet manufacturing process was established. The new sheet-configuration was consisted of the cathode with the grid of current collector, electrolyte sheet with or without mechanical support, and aluminum/lithium composite sheet anode. A sheet battery with a dimension of  $30\text{ mm} \times 30\text{ mm}$  showed good charge–discharge characteristics without any capacity fading at a current of 0.1 mA.

© 2009 Elsevier B.V. All rights reserved.

## 1. Introduction

All solid-state lithium batteries are a promising power source, which may overcome safety hazard issues of the conventional “lithium-ion battery (LIB)” [1]. Particularly, high ion-conductive inorganic solids electrolytes (ISEs) are the best candidate among alternatives to liquid electrolyte, because of their non-flammable nature even at high temperatures, a wide potential window, and uni-cationic character for ionic transport [2–8]. Among the ISEs,  $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$  (thio-LISICON) shows the conductivity as high as  $2.2 \times 10^{-3}\text{ Scm}^{-1}$  at room temperature, and is the most lithium-ion conductive solid [8]. Recently, we have developed a cell configuration of all solid-state batteries using the thio-LISICON. The self-assembled breathing interface improved the close contact between the anode and the electrolyte, and extremely high charge-and-discharge currents up to 1 C rate were achieved for the bulk-type solid-state cell. The Li–Al/ $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ / $\text{Mo}_6\text{S}_8$  cell showed the reversible capacity of  $80\text{ mAh g}^{-1}$  under a high current density of  $1.3\text{ mA cm}^{-2}$  at room temperature [9].

Excellent thermal stability of the ISE makes the large-scale sheet device possible to operate without safety protection accessories. Very little efforts, however, have been devoted to developing solid-

state sheet cells using inorganic solid electrolytes, because the brittle character of ISE prevents a fabrication of large and thin electrolyte films. There are three types of methods for sheet making process, (i) the electrolyte or cathode sheet with a mechanical support either by a plastic or metallic meshes, (ii) the electrolyte sheet with flexible support by polymer binder, and (iii) the electrolyte and cathode with the combination of the both support techniques [10–12]. However, sheet making process have never been optimized and no electrochemical characteristics have been reported.

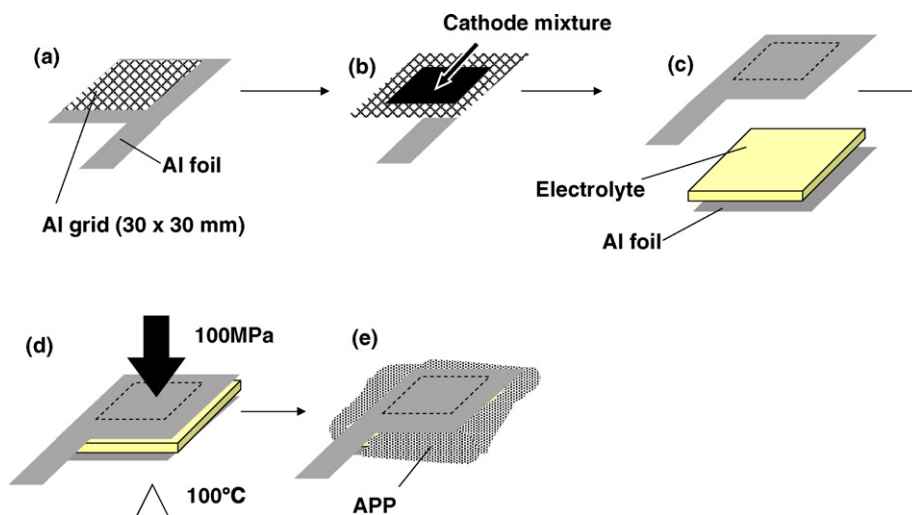
In the present study, the all solid-state sheet battery using lithium ISEs was constructed for the first time and the charge–discharge characteristics have been studied. Based on the Li–Al/thio-LISICON/ $\text{Mo}_6\text{S}_8$  system, the mesh-incorporated configuration and polymer binder method were used for sheet making process, and the solid-state sheet battery with a dimension of  $30\text{ mm} \times 30\text{ mm}$  was constructed.

## 2. Experimental

The thio-LISICON solid electrolyte,  $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$ , was synthesized as described previously [8]. The electrolyte was used after being pulverized into powder with an average grain size of 1–5  $\mu\text{m}$ . The cathode material,  $\text{Mo}_6\text{S}_8$ , with the Chevrel structure was prepared by reducing  $\text{Cu}_2\text{Mo}_6\text{S}_8$  (Nippon Inorganic Colour & Chemical) with concentrated HCl. The cathode mixture was obtained by mixing  $\text{Mo}_6\text{S}_8$ , thio-LISICON and acetylene black (Denki Kagaku Kogyo) in a gravimetric ratio of 70:30:3.5 using Fritsch P-7 planetary ball

\* Corresponding author.

E-mail address: [kanno@echem.titech.ac.jp](mailto:kanno@echem.titech.ac.jp) (R. Kanno).



**Fig. 1.** Schematic drawings of the sheet battery procedure. (a) Fabrication of the cathode current collector. (b) Coating of the cathode mixture. The initial recipe of the mixture was  $\text{Mo}_6\text{S}_8$  (240 mg),  $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$  (120 mg), and acetylene black (14 mg) to give a 50 mg of the cathode layer in the aluminum grid. (c) Cathode layer was placed on the electrolyte layer. The electrolyte slurry was the heptane solution of silicone (40 mg) and  $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$  (1.47 g). The initial coating thickness was 1 mm. The dimension of the electrolyte layer was 30 mm  $\times$  30 mm. The cathode layer was surrounded by the electrolyte layer charged in the margin of the cathode grid. (d) The cathode/electrolyte sheet was heated at 100 °C under 100 MPa to sinter the thio-LISICON and cure the silicone binder. (e) The cathode/electrolyte sheet was surrounded by an amorphous polypropylene.

milling apparatus. Lithium sheet (300  $\mu\text{m}$ -thick) and aluminum foil (12  $\mu\text{m}$ -thick) were used for the anode in sheet battery with the polymer binder. Heptane was used as a solvent for sheet fabrication; heptane was dried with activated molecular sieves (3A).

Cross-linkable polysiloxane (CY52-005, Dow Corning-Toray Silicone) was used as a sheet binder. The fabrication, and the conductivity of the composites, thio-LISICON and silicone, were previously reported [13]. The plastic mesh used for the self-standing electrolyte sheet was prepared by NBC Inc. The string was composed of polyarylate. The mesh has the thickness and openings of 19 and 25  $\mu\text{m}$ , respectively. The surface of the string was covered by a modified polyethylene terephthalate (PET, melting point ( $t_m$ ): 115 °C) with the coating thickness of 3–5  $\mu\text{m}$ .

Sheet batteries were fabricated in the conventional slurry coating process. Charge–discharge characteristics of the cells were examined at 25 °C with a constant current density of 0.1 or 0.5 mA in the potential range of 0.5–3.5 V. All the cell procedures and the characterization were carried out under dehydrated and oxygen-free argon atmosphere.

### 3. Results and discussion

#### 3.1. Sheet battery with binder composite

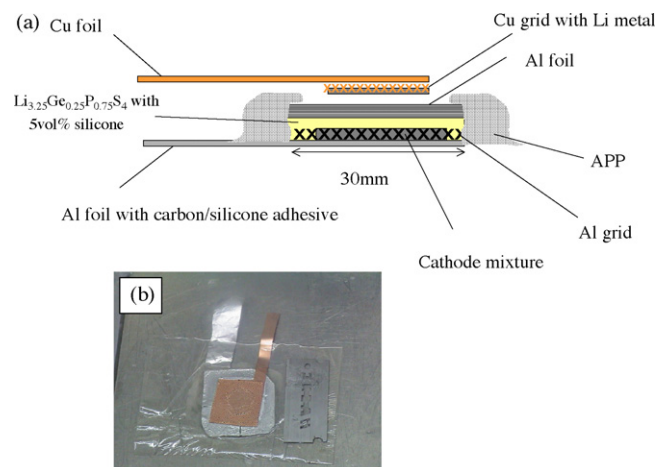
The cell configuration suitable for sheet battery was developed based on the cell,  $\text{Li}-\text{Al}/\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4/\text{Mo}_6\text{S}_8$  [9]. The important factors of constructing all solid-state battery are electronic-current collecting, high-ionic diffusion at the electrode/electrolyte interface, and protection of short circuit at the edges of the cells. The electronic-current collecting will be achieved by suitable designs of the current collector, and high lithium-ionic diffusion at the electrode/electrolyte will be attained by a close physical contact at the interface. To avoid short circuit at the edges of the cells, an insulator should be placed around the cathode/electrolyte sheet. Based on the above consideration, the sheet fabrication process for the all solid-state cell was examined. Fig. 1 shows the sheet fabrication procedure. The process was divided into several steps, (i) cathode fabrication on current collector, (ii) cathode-electrolyte stacking, (iii) sintering with polymer binder, and (iv) packaging. Each process proceeds as follows.

##### 3.1.1. Cathode fabrication on current collector

Optimization of electronic-current collector was examined for the cathode sheet. We made the cathode sheet using different current collectors; an aluminum foil, an aluminum grid, and a combination of both foil and grid. The foil for the current collector provides the simplest and the easiest procedure for making cathode film. The cathode component was directly coated on the aluminum foil. However, poor contact between the foil and cathode mixture often caused fabrication failure and/or short circuit. On the other hand, the aluminum grid could keep the powder inside the openings without any significant problems. We therefore used both the aluminum foil and the grid as the cathode current collector (Fig. 1(a)). The aluminum grid (0.1A0.15-M10, Katsurada Grating Co., Ltd.) having 0.1 and 0.15 mm for the thickness and openings, respectively, was cut in the square of 30 mm, and was glued on the foil using carbon/silicone adhesive. The cathode slurry was then coated on the grid with 5 mm margin along each brim (Fig. 2(b)).

##### 3.1.2. Cathode-electrolyte stacking

The electrolyte sheet was fabricated by a simple coating method. For the binder-composite system, the slurry of  $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$



**Fig. 2.** A schematic drawing (a) and the photograph (b) of the 30 mm  $\times$  30 mm sheet battery.

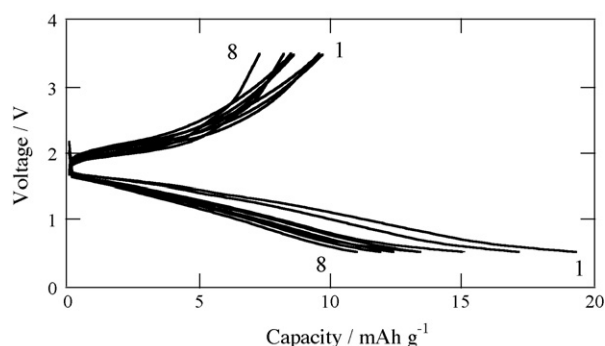


Fig. 3. The charge–discharge characteristics of the sheet battery examined at a current of 0.1 mA.

with 5 vol% of silicone binder was coated on an aluminum foil. The obtained electrolyte/anode–aluminum sheet was placed on the cathode sheet (Fig. 2(c)). The margin of the cathode grid was filled with the thio-LISICON/binder composite, which was effective to protect short circuit at circumference of the cell. The electrolyte sheet was also mechanically supported by the aluminum grid.

### 3.1.3. Sintering

Sintering of the cell was found to be efficient to improve cell characteristics. The effect was clarified by 10 mm Ø miniature sheet cell. The cell heated at 100 °C after the preparation showed 20% higher capacity than that obtained without heating. The sintering of the thio-LISICON caused closer contact and higher lithium-ion conduction. The heat treatment is also necessary for curing silicone binder. The stacked sheet composed of electrolyte and cathode was therefore treated at 100 °C under 100 MPa (Fig. 2(d)).

Polymer binder plays an important role for close and tight contact during the sintering process. However, the surface of the ISE particle is generally coated by the polymer binder [14], and the conductivity of the electrolyte layer decreases with the binder content because the binder components usually has low conductivity or almost insulating character. On the other hand, silicone (a cross-linkable polysiloxane) has two advantages for the ISE system. The liquid nature with low-viscosity makes the binder components flow into the void between the ISE particles, forming the granular polymer domain in the composite during the compression of the sheet [13] (Fig. 2(d)). This also makes tight contact between the ISE particles with polymer-free surface; high-ionic conduction is achieved without breaking the conduction pathway by the binder. The other advantage of the silicone is that hydrocarbons such as heptane are available as a solvent for the sheet formation process. High ion-conductive sulfides such as the thio-LISICON are not stable in solvents except for hydrocarbons [15]. As the liquid silicone is soluble to hydrocarbons, the homogeneous thio-LISICON/silicone slurry can be prepared. This makes conventional coating processes possible for the sheet battery formation.

### 3.1.4. Packaging

After the heat treatment, the edge of the cathode–electrolyte sheet was wrapped by a flexible amorphous polypropylene (Bistack-L, Chiba Fine Chemical) (Fig. 1(e)) to avoid short circuit during the rest of the procedure. A copper grid (0.05Cu0.18-M15NF, Katsurada Grating Co., Ltd.) having 0.05 and 0.18 mm for the thickness and openings, respectively, and the lithium sheet was placed on the cathode/electrolyte sheet. The sheet cell configuration is shown in Fig. 2(a). The cell was then sealed in a steam barrier transparent bag (GX-film, Toppan). Fig. 2(b) shows the photograph of the sheet cell.

Fig. 3 shows the charge–discharge characteristics at a current of 0.1 mA. The energy density of the sheet battery was 0.25 Ah kg<sup>-1</sup>

(0.35 Wh kg<sup>-1</sup>) based on the parameters, 1.4 V, 11 mAh g<sup>-1</sup>, 1.527 g and 35 mg, for the average voltage, discharge capacity per weight of active material in positive electrode, and total weight of the sheet battery, and weight of active material, respectively. Although the capacity is much lower than that expected, the sheet cell showed good capacity retention. The charge–discharge performance of the sheet battery increased with the increase in the pressure applied to the sheet battery and also with the adhesion area of the battery. This indicates that the contact between active material and solid electrolyte is important, and rather low capacity values of the sheet battery clarify the problems of the contact between the ceramic components. Although further efforts to reduce the contact resistance are necessary, we successfully indicated the possibility of industrial manufacturing process of all-solid sheet battery. The small capacity indicated that only a part of the cathode layer participates in the charge–discharge reactions, and this might be solved by optimizing sheet fabrication process.

### 3.2. Sheet battery with plastic mesh

Mechanical support by a plastic mesh provides a self-standing ISE sheet, which also makes the sheet manufacturing process easier. Total thickness required for the electrolyte sheet would be approximately 10–20 μm, which is similar to the thickness of a conventional separator of LIB. Thanks to the state of the art development of weaving, the thinnest plastic mesh has the thickness less than 20 μm with an opening area ratio over 70%. This makes mesh-incorporated ISE sheet possible.

We first fabricated mesh-incorporated sheet with polymer binder. However, the mechanical strength of the electrolyte sheet was not strong enough to handle for further fabrication process. The granular polymer domain provided the polymer-free openings, where the poor contact between the mesh string and thio-LISICON caused cracks in the sheet. The simple combination of the polymer binder and the plastic mesh was not suitable for the practical ISE sheet. We therefore designed the self-standing ISE sheet with a combination of the ISE and an adhesive polymer mesh. On the surface of the mesh string, a modified-PET was coated with a thickness of 3–5 μm. Inside the openings, polymer-free ISE particles occupied, and this gives conductive openings surrounded by the binder. The mesh string and the thio-LISICON were bound tightly after a heat treatment above the melting point ( $t_m$ ) of the binder. Very good contact between the ISE particles was obtained, and the advanced combination of ISE and adhesive mesh provided self-standing sheet. The thickness of the electrolyte sheet was around 100 μm.

The new sheet design has additional advantages for the sheet fabrication. For the conventional mixing method of polymer binder with sulfide ISE, polar solvents such as THF or acetone could not be used because of poor stability of the ISEs against these solvents [15], and this limits the variety of candidate materials for the

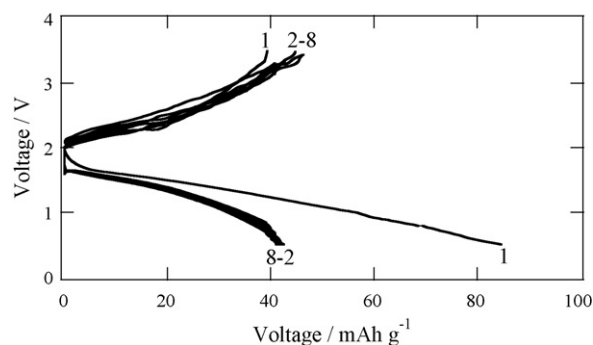


Fig. 4. The charge–discharge characteristics of the test cell using the advanced combination ISE sheet examined at a current density of 0.64 mA cm<sup>-2</sup>.

binder. The new method allows the variations of solvent available for sheet fabrication. For example, two different solvents are separately used; one for coating the mesh string with binder, and the other for preparing ISE slurry.

The self-standing electrolyte sheet makes simple stacking process possible for the cell fabrication. We examined the mesh-incorporated design using a test cell with the sample diameter of 10 mm  $\varnothing$ . The electrolyte layer was placed on the cathode layer. Then Li–Al powder alloy layer was placed on the electrolyte/cathode stacked layer. Fig. 4 shows the charge–discharge characteristics of the cell with a current density of 0.64 mA cm<sup>-2</sup>. The cell showed rather good cycling characteristics, which indicates that the coated-mesh is electrochemically stable. The polymer mesh might stabilize the electrolyte sheet mechanically and release the micro strain between the ceramic particles during the charge–discharge cycle.

#### 4. Summary

The prototype configuration and manufacturing process was established for the all solid-state battery using the thio-LISICON solid electrolyte. The charge–discharge characteristics of the sheet battery indicated the possibility of large-scale manufacturing of the all solid system. Our results may solve the safety hazard issue of the current lithium-ion battery and open new technology fields of ceramic all solid-state battery for practical application. The all solid-state sheet battery is becoming a promising candidate for large-scale batteries.

#### Acknowledgements

This work was supported partly by a grant from The Ministry of Economy, Trade and Industry of Japan, and by a grant-in-aid from The Ministry of Education, Culture, and Sports, Science and Technology of Japan.

#### References

- [1] D.H. Doughty, S.C. Levy, The 36th Battery Symposium in Japan, Kyoto, 1995, p. 1.
- [2] H. Wada, M. Menetrier, A. Levasseur, P. Hagenmuller, *Mater. Res. Bull.* 18 (1983) 189.
- [3] R. Mercier, J.P. Malugani, B. Fahys, G. Robert, *Solid State Ionics* 5 (1981) 663.
- [4] J.H. Kennedy, Y. Yang, *J. Electrochem. Soc.* 133 (1986) 2437.
- [5] J.H. Kennedy, Y. Yang, *J. Solid State Chem.* 69 (1987) 252.
- [6] J.H. Kennedy, Z. Zhang, *Solid State Ionics* 28/30 (1988) 726.
- [7] N. Aotani, K. Iwamoto, K. Takada, S. Kondo, *Solid State Ionics* 68 (1994) 35.
- [8] R. Kanno, M. Murayama, *J. Electrochem. Soc.* 148 (2001) A742.
- [9] R. Kanno, M. Murayama, T. Inada, T. Kobayashi, K. Sakamoto, N. Sonoyama, A. Yamada, S. Kondo, R. Kanno, *Electrochem. Solid-State Lett.* 7 (2004) A455.
- [10] R.H.Y. Subban, A.K. Arof, *J. Power Sources* 134 (2004) 211.
- [11] T. Inada, K. Takada, A. Kajiyama, M. Kouguchi, H. Sasaki, S. Kondo, M. Watanabe, *Proceedings of the 18th International Japan-Korea Seminar on Ceramics*, 2001, p. 76.
- [12] T. Hara, N. Yasuda, M. Nagata, S. Kondo, T. Sotomura, *Polym. Adv. Technol.* 4 (1993) 194.
- [13] T. Inada, K. Takada, A. Akihisa, M. Kouguchi, H. Sasaki, S. Kondo, M. Watanabe, M. Murayama, R. Kanno, *Solid State Ionics* 158 (2003) 275.
- [14] S. Skaarup, K. West, B. Zachau-Christiansen, *Solid State Ionics* 28–30 (1998) 975.
- [15] T. Inada, K. Takada, A. Kajiyama, H. Sasaki, S. Kondo, M. Watanabe, M. Murayama, R. Kanno, *J. Power Sources* 119–121 (2003) 948.