Short communication

Characterization of all-solid-state lithium secondary batteries using Cu$_x$Mo$_6$S$_{8-y}$ electrode and Li$_2$S–P$_2$S$_5$ solid electrolyte

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ABSTRACT

All-solid-state cells were fabricated using Cu$_x$Mo$_6$S$_{8-y}$ Chevrel-phase as an active material and Li$_2$S–P$_2$S$_5$ glass–ceramics as a solid electrolyte. The cells showed good cycle performance with a constant capacity of about 100 mAh g^{-1} for 2000 cycles at the current density of 1.28 mA cm^{-2} at room temperature. The reaction mechanism in the all-solid-state cells was investigated using X-ray diffraction (XRD). The XRD pattern after the 100th charge was almost identical to that before cycling; it is therefore considered that the retention of the crystal structure during cycling brings about a good cycle performance. The use of Cu$_x$Mo$_6$S$_{8-y}$ as an electrode and Li$_2$S–P$_2$S$_5$ glass–ceramics as a solid electrolyte led to the formation of a good solid–solid interface using impedance spectroscopy. All-solid-state cells using Cu$_x$Mo$_6$S$_{8-y}$ as an active material and the 70Li$_2$S·30P$_2$S$_5$ (mol%) glass–ceramic as a solid electrolyte worked at a high current density of 12.8 mA cm^{-2} at a high temperature of 160 °C and retained a reversible capacity of about 270 mAh g^{-1} for 10 cycles.

1. Introduction

Lithium ion batteries have been widely used as power sources of various mobile electronic devices. Liquid electrolytes using an organic solvent are mainly used for commercially available batteries. It is considered that the use of non-flammable solid electrolytes instead of flammable liquid electrolytes engenders the high safety and high reliability of batteries. Using sulfide electrolytes, 3-V type all-solid-state lithium batteries have been studied [1–5]. All-solid-state cells of In/Li$_2$S–P$_2$S$_5$ glass–ceramic/LiCoO$_2$ showed an excellent cycle performance with a high capacity of 100 mAh g^{-1} for 500 cycles [2,3]. However, one issue that must be resolved for all-solid-state cells is improvement of the charge–discharge performance at a current density higher than 1 mA cm^{-2}. Results presented herein demonstrate that the cells using LiCoO$_2$ coated with Li$_4$Ti$_5$O$_{12}$ and Li$_2$SiO$_3$ thin-films can function at high current densities of more than several milliamperes per square centimeter [4,5]. To achieve high rate performance of all-solid-state batteries, electrode materials suitable for batteries with high power density are needed: solid electrolytes with high Li$^+$ ion conductivity.

We developed glass-based solid electrolytes: the Li$_2$S–P$_2$S$_5$ glass–ceramics exhibited high Li$^+$ ion conductivity of more than 10^{-3} S cm^{-1} at room temperature [6,7]. As described above, the Li$_2$S–P$_2$S$_5$ glass–ceramics are promising electrolytes for all-solid-state batteries.

A so-called Chevrel-phase compound, Cu$_x$Mo$_6$S$_{8-y}$, as one example of M$_x$Mo$_6$S$_8$ (M = Cu, Ni, Fe, etc.), has been studied as a positive electrode material in lithium batteries using conventional liquid electrolytes [8–11]. In fact, Cu$_x$Mo$_6$S$_{8-y}$ exhibits high electronic conductivity and a high Li diffusion coefficient; lithium ions are intercalated into Cu$_x$Mo$_6$S$_{8-y}$ at high current densities. Kanno et al. [12] reported that Mo$_6$S$_8$ obtained by leaching copper from Cu$_2$Mo$_6$S$_8$ with concentrated HCl solution was applied to the electrode of all-solid-state cells. The cells of Li–Al/thio-LISICON/Mo$_6$S$_8$ showed good cycle performance at 1.3 mA cm^{-2}.

Enhancement of the rate performance of lithium batteries was achieved by elevating the batteries' operating temperatures. High-temperature batteries with molten salt electrolytes reportedly show high-rate performance [13,14]. Operation at high temperatures was suggested in all-solid-state Cu batteries using the Cu$_x$Mo$_6$S$_{8-y}$ Chevrel-phase electrode [15]. Therefore, the Chevrel-phase is a promising electrode material for achieving high-rate and high-temperature performances in all-solid-state lithium secondary batteries. If the all-solid-state lithium batteries can function at temperatures higher than 100 °C, at which it is difficult for the batteries using conventional liquid electrolytes to function, the diversification of lithium battery application to devices is expected, along with rate performance improvement.

In this work, all-solid-state cells of Li–In/Li$_2$S–P$_2$S$_5$ glass–ceramic/Cu$_x$Mo$_6$S$_{8-y}$ were fabricated. The charge–discharge

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reaction mechanism of $Cu_xMo_6S_{8-y}$ in the cells was analyzed using XRD measurements for the working electrode after charge–discharge tests. Electrochemical properties were investigated using charge–discharge measurements and impedance spectroscopy. Galvanostatic tests of the cells were performed at 25 °C and 160 °C at current densities higher than 1 mA cm^{-2}.

2. Experimental

We used Li_2S–P_2S_5 glass–ceramics as solid electrolytes for all-solid-state electrochemical cells. The 80Li_2S·20P_2S_5 (mol%) glassy powders were prepared by continuous mechanical milling (10 h) for the mixture of Li_2S (Idemitsu Kosan Co. Ltd. 99.9%) and P_2S_5 (Aldrich, 99%) crystals with a planetary ball mill apparatus (Pulverisette 7; Fritsch GmbH). The rotation speed was fixed at 510 rpm at room temperature. The obtained glassy powders were heated at 210 °C for 4 h to obtain the 80Li_2S·20P_2S_5 glass–ceramics [6]. The 70Li_2S·30P_2S_5 glass–ceramic electrolyte was prepared using almost identical processes to those for the 80Li_2S·20P_2S_5 glass–ceramic one. Mechanical milling was performed at a rotation speed of 370 rpm for 8 h [7]. We used the $Cu_xMo_6S_{8-y}$ powders (Nippon Inorganic Colour & Chemical Co. Ltd.) as an active material. The powders' particle size was examined using a scanning electron microscope: it was about 5 μm. Electric conductivity of $Cu_xMo_6S_{8-y}$ was about 1 S cm^{-1}, as measured by DC polarization. All-solid-state electrochemical cells were fabricated as follows: the composite electrode was prepared from $Cu_xMo_6S_{8-y}$, 80Li_2S·20P_2S_5 glass–ceramic and acetylene-black with the weight ratio of 20:30:3. The obtained composite electrode (15 mg), used as a working electrode layer, and 80Li_2S·20P_2S_5 glass–ceramic or 70Li_2S·30P_2S_5 glass–ceramic (80 mg), used as an electrolyte layer, were placed in a polycarbonate tube (ϕ = 10 mm) and were pressed together under 360 MPa. Then Li–In alloy, used as a counter electrode, was attached on the solid electrolyte layer; the three-layered pellet was pressed under 120 MPa. The obtained pellet was sandwiched between two stainless steel disks, which were used as current collectors. All processes described above were carried out in a dry Ar glove box.

The electrochemical impedance measurements of the Li–In/80Li_2S·20P_2S_5 glass–ceramic/$Cu_xMo_6S_{8-y}$ cells were carried out using an impedance analyzer (SI 1260; Solartron Analytical) before and after charge–discharge tests under a constant current density of 1.28 mA cm^{-2} at 25 °C. The cells were charged and discharged at constant current densities of 1.28 mA cm^{-2} at 25 °C and 12.8 mA cm^{-2} at 160 °C in an Ar atmosphere using a charge–discharge measuring device (BTS-2004; Nagano Co.). To analyze the structure of the working electrode, the XRD measurements (Cu Kα) of the working electrode after charge–discharge tests were conducted in an Ar atmosphere using a diffractometer (M18XHF22-SRA; Mac Science Ltd.).

3. Results and discussion

Fig. 1 portrays the charge–discharge curves (a) and the cycle performance (b) of an all-solid-state cell of Li–In alloy/80Li_2S·20P_2S_5 glass–ceramic/$Cu_xMo_6S_{8-y}$ at the current density of 1.28 mA cm^{-2} at room temperature. The cutoff voltage is between 0 V and 3.0 V (vs. Li–In). In this figure, the ordinate axis on the left side represents the cell potential vs. Li–In electrode (counter electrode); that on the right side represents the potential vs. Li electrode which was calculated on the basis of potential difference between Li–In and Li electrodes [1]. The all-solid-state cell works as a lithium secondary battery at the current density of 1.28 mA cm^{-2}. Although an irreversible capacity is observed during an initial few cycles in
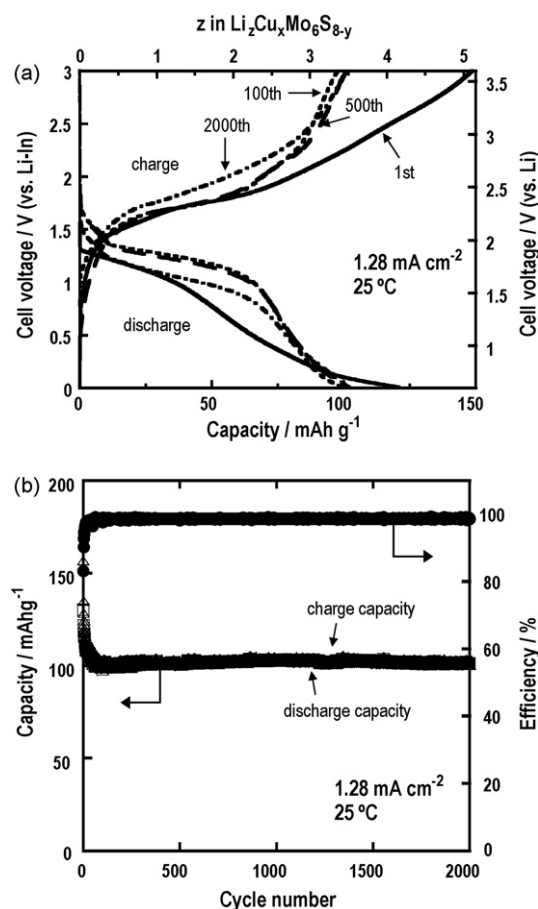

Fig. 1. Charge–discharge curves (a) and cycle performance (b) of the all-solid-state cells of Li–In/80Li_2S·20P_2S_5 glass–ceramic/$Cu_xMo_6S_{8-y}$ at 25 °C. The cutoff voltage is 0–3 V (vs. Li–In).

the cell, subsequently, the cell shows the charge–discharge efficiency of about 100% up to the 2000th cycle. One plateau at about 1.9 V (vs. Li) observed for the discharge process in the cell and the plateau voltage is almost identical to that reported in electrochemical cells with liquid electrolytes [9]. The Li–In/$Cu_xMo_6S_{8-y}$ cell using the 80Li_2S·20P_2S_5 glass–ceramic electrolyte shows a good cycle performance, with capacities of about 100 mAh g^{-1} for 2000 cycles.

Fig. 2 shows the change of XRD patterns for the working electrode using $Cu_xMo_6S_{8-y}$ before and after charge–discharge tests. The diffraction peaks before cycling (a) are attributed to $Cu_xMo_6S_{8-y}$ [16]. The XRD patterns for the working electrode after the first charge (b) and the 100th charge (c) are almost identical to the pattern before cycling. Results show that a Chevrel-phase, which has a stable three-dimensional framework based on Mo_6S_8 cluster, is retained after 100 cycles, suggesting that retaining the crystal structure during cycling engenders good cycle performance, as presented in Fig. 1.

Fig. 3 portrays AC impedance plots of the all-solid-state cells of Li–In alloy/80Li_2S·20P_2S_5 glass–ceramic/$Cu_xMo_6S_{8-y}$. Measurements were carried out before cycling and after discharging to 0 V (vs. Li–In) and charging to 3 V (vs. Li–In) at the current density of 1.28 mA cm^{-2}. The cell resistance is about 130 Ω before cycling. The impedance profiles of the cells after the first charge and discharge are almost identical to the profile before cycling. As the number of cycles increases, the profiles after the discharge process become almost identical to those before cycling, but one semicircle of the low-frequency region is observed after the charge
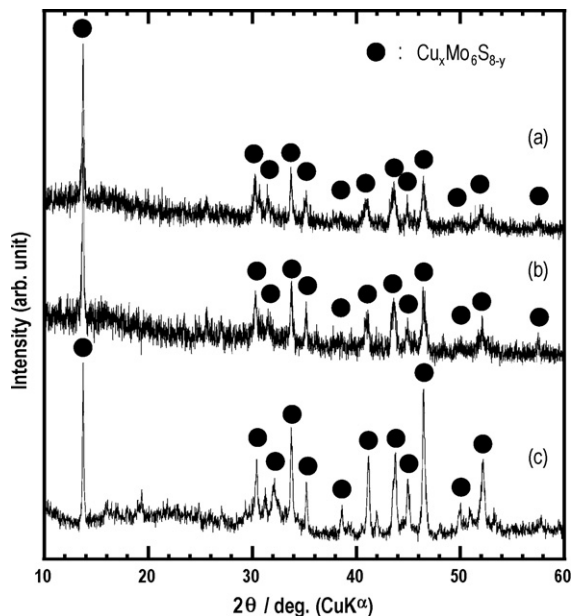
Fig. 2. XRD patterns for the working electrode using $Cu_xMo_6S_{8-y}$ before cycling (a), after the first charge (b), and after the 100th charge (c).

process. Nevertheless, the semicircle vanishes when the cells are discharged again. The total cell resistance after hundreds of cycles is almost identical to that before cycling. Therefore, we infer that the cells show a long cycle life. Batteries using $LiCoO_2$ as an electrode and $Li_2S–P_2S_5$ glass–ceramics as a solid electrolyte showed a large resistance after the first charge process [5]. Reportedly, the resistance results from formation of a high-resistance layer between the electrode and the electrolyte [4,5]. On the other hand, large resistance was not found in the cells using $Cu_xMo_6S_{8-y}$ as an electrode and $Li_2S–P_2S_5$ glass–ceramics as a solid elec-
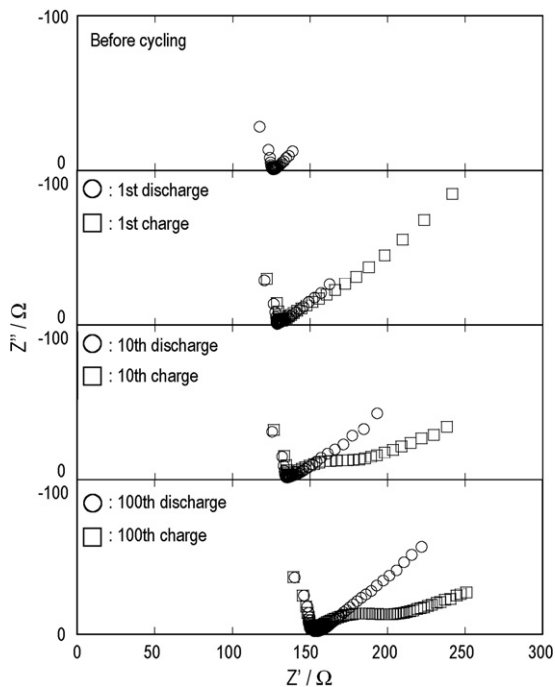
Fig. 3. AC impedance plots of the all-solid-state cells of Li–In/80Li_2S·20P_2S_5 glass–ceramic/$Cu_xMo_6S_{8-y}$ before and after cycling. The cells were charged and discharged at 0–3 V (vs. Li) at the current density of 1.28 mA cm^{-2} at 25 °C.

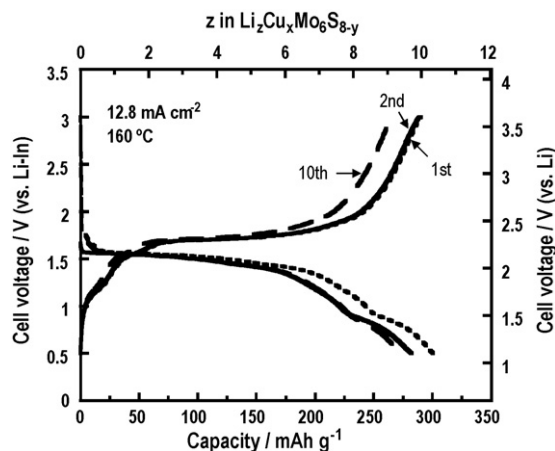**Fig. 4.** Charge–discharge curves of the all-solid-state cells of Li–In/70Li_2S·30P_2S_5 glass–ceramic/$Cu_xMo_6S_{8-y}$ with cutoff voltage of 0.5–3.0 V (vs. Li–In) at the current density of 12.8 mA cm^{-2} at 160 °C.

trolyte, indicating that a good solid–solid interface between the $Cu_xMo_6S_{8-y}$ electrode and the $Li_2S–P_2S_5$ glass–ceramic electrolyte is formed.

Fig. 4 shows charge–discharge curves of the all-solid-state cells of Li–In alloy/70Li_2S·30P_2S_5 glass–ceramic/$Cu_xMo_6S_{8-y}$ at the current density of 12.8 mA cm^{-2} at 160 °C. Here we used 70Li_2S·30P_2S_5 glass–ceramic [7], which exhibits higher lithium ion conductivity than the 80Li_2S·20P_2S_5 glass–ceramic [6]. The Li–In/$Cu_xMo_6S_{8-y}$ cell is charged and discharged even at a high current density of 12.8 mA cm^{-2} at 160 °C. The cell retains a high reversible capacity of about 270 mAh g^{-1} after 10 cycles. Few reports in the relevant literature describe the electrochemical performance of a lithium battery at temperatures higher than 100 °C. This is the first report of an all-solid-state cell using sulfide electrolytes with high Li$^+$ ion conductivity operating at the considerably high temperature of 160 °C. Results presented herein demonstrate that the all-solid-state cell works as a rechargeable lithium battery with high rate performance.

4. Conclusions

All-solid-state cells of Li–In/$Li_2S–P_2S_5$ glass–ceramic/$Cu_xMo_6S_{8-y}$ were fabricated. A cell with 80Li_2S·20P_2S_5 glass–ceramic electrolyte showed excellent cycle performance with the reversible capacity of about 100 mAh g^{-1} for 2000 cycles. The XRD pattern of the electrode after 100 cycles was almost identical to that before cycling, indicating that the crystal structure of $Cu_xMo_6S_{8-y}$ was retained during cycling. The total resistance of the cell after the 100th cycle was almost identical to that before cycling. These results demonstrate that the cell showed good cycle performance. The Li–In/$Cu_xMo_6S_{8-y}$ cell with the 70Li_2S·30P_2S_5 glass–ceramic as a solid electrolyte was charged and discharged at a high current density of 12.8 mA cm^{-2} at 160 °C. The cell showed a high reversible capacity of about 270 mAh g^{-1} after 10 cycles.

Acknowledgements

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