All Solid-state Lithium Secondary Batteries Using High Lithium Ion Conducting Li_2S–P_2S_5 Glass-Ceramics

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All solid-state cells of In/$LiCoO_2$ using the $80Li_2S{\cdot}20P_2S_5$ (mol%) glass-ceramics with high ambient temperature conductivity of about 10^{-3} S cm^{-1} as a solid electrolyte were fabricated, and the cell performance was investigated. Although an irreversible capacity was observed at the 1st cycle, the solid-state cell exhibited excellent cycling performances with the reversible charge-discharge capacities of about 100 mAh g^{-1} even after 200 cycles.

Lithium secondary batteries are widely prevalent as a power source for portable electronic devices, because these batteries have superior properties like high energy density, light weight, and long life. However, these batteries often use liquid electrolytes with organic solvents and need the safety mechanism such as a separator to prevent liquid electrolytes from igniting and leaking. If it is possible to replace liquid electrolytes with solid electrolytes, those safety problems would be effectively solved.

Melt quenched sulfide glasses in the systems Li_2S–P_2S_5 and Li_2S–SiS_2 have been investigated as solid electrolytes for lithium secondary batteries because of their high lithium ion conductivity.[1–4] Recently, we have succeeded in preparing those sulfide lithium ion conducting glasses as fine powders by mechanical milling at room temperature,[5,6] and confirmed that all solid state cells with these glassy powders as solid electrolytes work as lithium secondary batteries.[7,8] New glass-ceramics have also been obtained by heating the $80Li_2S{\cdot}20P_2S_5$ (mol%) mechanically milled glass; the glass-ceramics exhibit high ambient temperature conductivity around 10^{-3} S cm^{-1}, which is higher than that of the pristine glass.[9,10] A crystal precipitated in the glass-ceramics is proved to be similar to highly conductive thio-LISICON,[11] which is a series of sulfide crystalline solid electrolytes such as Li_4GeS_4–Li_3PS_4 reported by Kanno et al.[12]

In the present study, we have assembled all solid-state cells of In/$LiCoO_2$ using the $80Li_2S{\cdot}20P_2S_5$ (mol%) glass-ceramics as a solid electrolyte. Cell performances as lithium secondary batteries are examined under a constant current density at room temperature.

Glassy powders of $80Li_2S{\cdot}20P_2S_5$ (mol%) were prepared by mechanical milling for 20 h; detailed experimental procedures were described in our previous reports.[6,9,10] The obtained glassy powders were gradually heated up to 230 °C and kept the temperature for 4 h, and gradually cooled down to room temperature in an Ar atmosphere to yield highly conductive glass-ceramics.

Laboratory-scale solid-state cells of In/$LiCoO_2$ using the glass-ceramics obtained as a solid electrolyte were fabricated as follows. In order to achieve smooth electrochemical reaction in all solid-state cells, we prepared composite cathode materials from following three kinds of powders: the active material, the solid electrolyte powder providing lithium ion conduction path, and the acetylene black providing electron conduction path. The composite cathode materials were obtained by mixing of $LiCoO_2$, the glass-ceramics and acetylene black with the weight ratio of 20 : 30 : 3. The composite powder (20 mg) as a cathode and the glass-ceramics 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 with a thickness of 0.1 mm as an anode was pressed under 2500 kg cm^{-2} on the pellet. The cell was charged and discharged under a constant current density of 64 μA cm^{-2} in order to evaluate cycling performance. This measurement was carried out at room temperature in an Ar atmosphere.

Figure 1 shows the X-ray diffraction patterns of the $80Li_2S{\cdot}20P_2S_5$ samples mechanically milled for 20 h before and after the heat treatment at 230 °C. Although the diffraction peaks due to Li_2S crystal are slightly observed, the $80Li_2S{\cdot}20P_2S_5$ powders before the heat treatment are almost amorphous. After the heat treatment, new diffraction peaks are observed. Kanno et al. have reported the XRD patterns of thio-LISICON crystals in the system Li_4GeS_4–Li_3PS_4 prepared by solid-phase reaction.[12] From the structural point of view, the thio-LISICON $Li_{4-x}Ge_{1-x}P_xS_4$ is divided into three composition

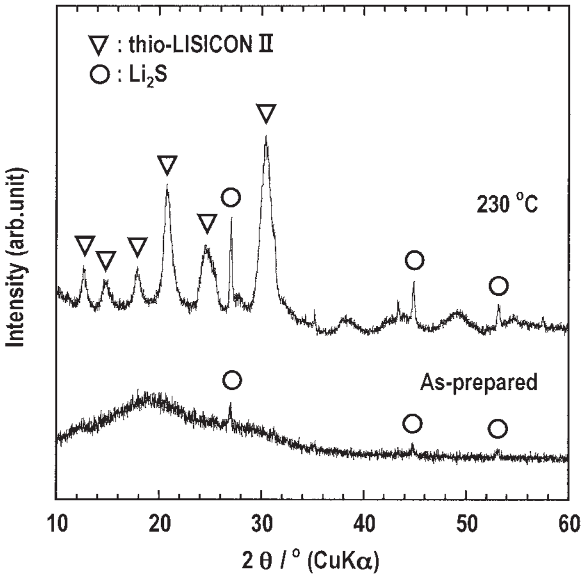

Figure 1. X-ray diffraction patterns of the $80Li_2S{\cdot}20P_2S_5$ samples mechanically milled for 20 h before and after the heat treatment at 230 °C. Open circles and triangles denote Li_2S and thio-LISICON II, respectively.

regions: region I ($0 < x \leqq 0.6$), region II ($0.6 < x < 0.8$), and region III ($0.8 \leqq x < 1.0$). The thio-LISICON phase in region II has a special monoclinic superstructure and shows much higher conductivities over 10^{-3} S cm^{-1} at room temperature than the other phases (regions I and III). The XRD pattern of the glass-ceramics after heat treatment as shown in Figure 1 is very similar to that of the thio-LISICON phase in region II (thio-LISICON II), suggesting that the precipitated crystalline structure is similar to the structure of thio-LISICON II. We presume that the precipitated crystal is the Li-rich $Li_{3+5y}P_{1-y}S_4$ ($0.04 < y < 0.08$) phases with a lack of phosphorus.[11] The thio-LISICON II phase has not been obtained by solid-phase reaction in the Li_2S–P_2S_5 binary system from our preliminary experiments and, therefore, this crystalline phase may be only obtained from the mechanically milled glassy powders. The pellet of the glass-ceramics exhibited the ambient temperature conductivity of 7.2×10^{-4} S cm^{-1} at room temperature, which is higher than 1.7×10^{-4} S cm^{-1} for the pellet of the pristine glassy powder.

Figure 2 shows the charge and discharge curves of the In/$80Li_2S{\cdot}20P_2S_5$ glass-ceramics/$LiCoO_2$ cell at the 1st and 200th cycles. In this measurement, the cell was charged up to $x = 0.4$ in $Li_{1-x}CoO_2$ and discharged to 2 V at 1st cycle, and then it was charged up to $x = 0.3$ in $Li_{1-x}CoO_2$ and discharged to 2 V at 2nd cycle. After the 3rd cycle, the cell was charged and discharged between the maximum voltage of the 2nd cycle and 2 V. At the 1st cycle, a relatively large irreversible capacity is observed. There are two possibilities for this large irreversible capacity; one is that lithium would not sufficiently extracted from $LiCoO_2$ in the charge process and the other is that all of lithium would not be extracted from Li–In alloy in the discharge process. At the present stage, we have not decided which of them is mainly responsible for the irreversible capacity. After the 2nd cycle, the irreversible capacity dramatically decreases and the charge-discharge capacity gradually increases with charge-discharge cycle number. The charge-discharge curves at the 200th cycle shown in Fig. 2 indicate that the all solid-state cell has the reversible capacity of about 100 mAh g^{-1} and charge-discharge efficiency is almost 100% (no irreversible capacity). The charge-discharge profiles after the 50th cycle are almost the same as those of the 200th cycle. These results show that the In/$LiCoO_2$ cell using the $80Li_2S{\cdot}20P_2S_5$ glass-ceramics has an excellent cycling performance with no capacity loss up to the cycle number of 200. The advantage of the glass-ceramics in their high conductivity and dense microstructure without grain boundary, which was confirmed from SEM observation,[10] would promote smooth charge-discharge reaction in the solid/solid interface between electrolyte and electrode.

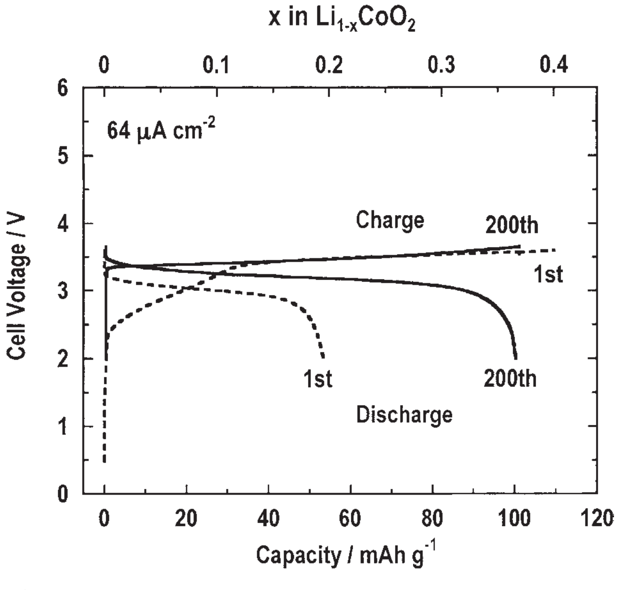

Figure 2. Charge and discharge curves for an all solid-state cell of In/$LiCoO_2$ with the $80Li_2S{\cdot}20P_2S_5$ glass-ceramics as a solid electrolyte at 1st and 200th cycles. The measurement was carried out at room temperature under a constant current density of 64 μA cm^{-2}.

In conclusion, all solid-state cells using the glass-ceramics derived from mechanically milled $80Li_2S{\cdot}20P_2S_5$ glassy powders worked as lithium secondary batteries and exhibited excellent cycling performance at room temperature. The glass-ceramics containing highly conductive thio-LISICON II crystal are suitable solid electrolytes for lithium secondary batteries.

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