

Design of composite positive electrode in all-solid-state secondary batteries with $\text{Li}_2\text{S-P}_2\text{S}_5$ glass–ceramic electrolytes

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Abstract

Composite positive electrodes for all-solid-state In/LiCoO_2 cells with $\text{Li}_2\text{S-P}_2\text{S}_5$ glass–ceramic electrolytes were designed in order to improve the high rate performances of the cells. The composite electrodes consisted of the active material, the solid electrolyte and carbon conductive additive powders. The cell with vapor grown carbon fiber (VGCF) as a conductive additive was charged and discharged at current densities of over 1 mA cm^{-2} , while the cell with acetylene black (AB) did not work as a rechargeable battery. The difference in the cell performances was explained from viewpoints of the morphology of the carbon additives. VGCF formed a more continuous electron conducting path in the composite positive electrode than AB. The cells without conductive additives were charged and discharged by increasing LiCoO_2 content in the composite positive electrode. Using a suitable morphology and amount of component powders for composite electrodes is a key to improve rate performances of all-solid-state secondary batteries.

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1. Introduction

All-solid-state lithium secondary batteries have been intensively studied as new power sources with high energy density, high safety and high reliability. Inorganic solid electrolytes with nonflammability are the most promising candidate to realize these solid-state batteries. Sulfide-based lithium ion conducting glasses have been reported to show high conductivities at room temperature [1–3]. In particular, $\text{Li}_2\text{S-SiS}_2$ -based glasses prepared by melt quenching exhibited high lithium ion conductivities of about $10^{-3} \text{ S cm}^{-1}$ at room temperature [4–6]. All-solid-state In/LiCoO_2 cells using these glasses as solid electrolytes exhibited excellent cycling performances as rechargeable batteries [6–8].

We reported that the glass–ceramics obtained by crystallization of the mechanically milled $\text{Li}_2\text{S-P}_2\text{S}_5$ glasses exhibited high lithium ion conductivities of about $10^{-3} \text{ S cm}^{-1}$ at room temperature [9,10]. All-solid-state In/LiCoO_2 cells with the $\text{Li}_2\text{S-P}_2\text{S}_5$ glass–ceramics kept high capacities of

100 mAh g^{-1} and high efficiencies of 100% over 200 cycles at a current density of $64 \mu\text{A cm}^{-2}$ at room temperature [11]. Positive electrodes in these solid-state cells are composed of the active material, the solid electrolyte and a conductive additive. Since it is not easy for lithium ions and electrons to conduct in the powder-compressed electrodes consisting of only the active material, the solid electrolyte and conductive additive powders are necessary to secure their conduction in the electrodes [12]. Thus, it is significant to design and control solid–solid interfaces among electrode components in order to improve high rate performance of all-solid-state cells. In our recent report, the effect of conductive additives such as carbon, titanium nitride and nickel in composite positive electrodes on the charge–discharge properties of all-solid-state cells was investigated [13].

In the present study, we focused on carbon conductive additives in composite positive electrodes for all-solid-state batteries. Two carbon materials with different morphologies has been selected; one is acetylene black (AB) as conventionally used nanoparticles (about 15 nm in size) and the other is vapor grown carbon fiber (VGCF) with 150 nm in diameter. The composite positive electrodes without conductive

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additives were also prepared. All-solid-state cells using the composite electrodes with and without two different kinds of carbon materials were assembled. The influence of carbon conductive additives on charge–discharge behaviors of the cells, especially under high current densities, was investigated.

2. Experimental

$\text{Li}_2\text{S}\text{-P}_2\text{S}_5$ glass–ceramics for solid electrolytes were prepared by mechanical milling and subsequent heat treatment [9–11]. Reagent-grade chemicals of Li_2S (Furuuchi Chemical, 99.9%) and P_2S_5 (Aldrich Chemical, 99%) were used as starting materials to prepare the $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$ (mol%) glass, whose composition was selected because the glass–ceramic exhibited high conductivity of $7.2 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature [9]. The mixture of these materials was mechanically milled under a rotating speed of 370 rpm for 20 h at room temperature. The obtained glassy powder was heated at 230°C to yield highly conductive glass–ceramics. All the processes were performed in a dry Ar-filled glove box ($[\text{H}_2\text{O}] < 1 \text{ ppm}$).

Laboratory-scaled solid-state cells were constructed as follows [11–13]. Powders of LiCoO_2 (Honjo Chemical), the $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$ glass–ceramic, and vapor grown carbon fiber (VGCF, Showa Denko) or acetylene black (AB, Denki Kagaku Kogyo) were used to prepare composite positive electrodes. The powders were weighed as shown in Table 1, and the composite electrodes were obtained by dry-mixing with agate mortar for 30 min. An indium foil (Furuuchi Chemical, 99.999%) was used as a negative electrode. The composite positive electrode (20 mg) and the glass–ceramic solid electrolyte (80 mg) were together pressed under 3700 kg cm^{-2} in a polycarbonate tube ($\varphi = 10 \text{ mm}$), and then the indium foil was pressed under 2500 kg cm^{-2} on the obtained pellet. The three-layered pellet was sandwiched and held by two stainless-steel disks as current collectors. The cells were charged and discharged using a charge–discharge measuring device (BTS-2004, Nagano). Cycling performances were evaluated under constant current densities of 64 and $1280 \mu\text{A cm}^{-2}$ at room temperature in an Ar atmosphere.

Table 1

Composition of composite positive electrodes, conductive additives and current densities used in charge–discharge measurements

Cell composition of composite positive electrode $\text{LiCoO}_2\text{:SE:conductive additive}^a$ (wt. ratio)	Conductive additive	Current density ($\mu\text{A cm}^{-2}$)
A	VGCF	64
B	VGCF	1280
C	AB	1280
D	–	64
E	–	64
F	–	1280

^a SE: the $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$ glass–ceramic solid electrolyte.

Compositions of composite positive electrodes, conductive additives and current densities used in these measurements are listed in Table 1.

3. Results and discussion

Composite positive electrodes for all-solid-state cells were prepared by mixing LiCoO_2 , the $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$ glass–ceramic electrolyte and a carbon conductive additive of VGCF or AB. FE-SEM observation suggested that AB with average particle size of about 15 nm formed submicron-sized agglomeration, whereas fibrous VGCF with average diameter of about 150 nm was randomly dispersed [13].

Fig. 1 shows the first charge and discharge curves of all-solid-state In/LiCoO_2 cells using the composite positive electrodes with different conductive additives. Dotted, solid and dashed lines respectively denote the cells A, B and C shown in Table 1. The cell A with VGCF operating at a current density of $64 \mu\text{A cm}^{-2}$ shows a discharge plateau of about 3.2 V and a discharge capacity of about 80 mAh g^{-1} under a cut off voltage of 2.0 V. The cell B with VGCF is charged and discharged even at a current density of $1280 \mu\text{A cm}^{-2}$, although the drop of the discharge potential is observed. The cell B shows a discharge plateau of about 2.8 V and a discharge capacity of about 75 mAh g^{-1} under a cut off voltage of 1.5 V. The cell C with AB is also charged and discharged at a current density of $1280 \mu\text{A cm}^{-2}$. However, the potential drop of the cell is larger than that of the cell with VGCF. The cell C shows a discharge plateau of about 2.0 V and a discharge capacity of about 45 mAh g^{-1} up to 1.5 V.

Fig. 2 shows the discharge capacities and charge–discharge efficiencies of all-solid-state In/LiCoO_2 cells with conductive additives as a function of cycle number. Filled and open marks respectively denote the discharge capacities and charge–discharge efficiencies. Circles, diamonds and triangles denote the cells A, B and C, respectively. Until the second cycle, all the cells were charged up to $x = 0.40$ in $\text{Li}_{1-x}\text{CoO}_2$ (110 mAh g^{-1}), and then the cell A was discharged to 2.0 V

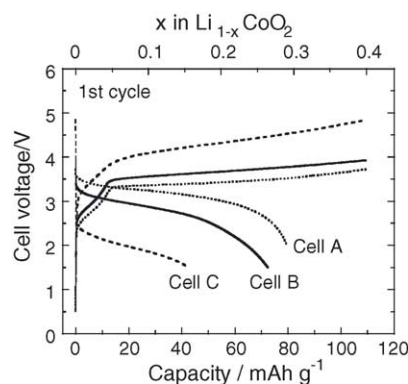


Fig. 1. First charge and discharge curves of all-solid-state In/LiCoO_2 cells with conductive additives. Detailed conditions of the cells A, B and C are described in Table 1.

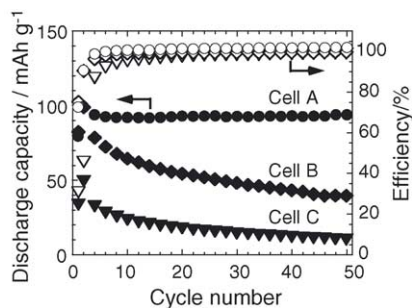


Fig. 2. Discharge capacities and charge–discharge efficiencies of all-solid-state In/LiCoO₂ cells with conductive additives as a function of cycle number.

and the cells B and C were discharged to 1.5 V. After the third cycle, charge–discharge cycles were repeated between the maximum charge voltage of the second cycle and 2.0 or 1.5 V. At the second cycle, the cells A and B exhibit the reversible capacities of about 100 mAh g⁻¹, while the cell C exhibits the capacity of about 50 mAh g⁻¹. After the third cycle, high discharge capacities of about 100 mAh g⁻¹ and high charge–discharge efficiencies of 100% are maintained for the cell A. We confirmed that the cell A showed an excellent cycling performance with no capacity losses up to the 200th cycle. In contrast, discharge capacities of the cell B monotonically decrease with an increase in cycle number, although high charge–discharge efficiencies of 100% are obtained. The cell C exhibits lower discharge capacities than the cell B. At the 50th cycle, the discharge capacities of the cells B and C are respectively about 40 and 10 mAh g⁻¹. The cells B and C were charged and discharged at a current density of 64 μA cm⁻² after operating at 1280 μA cm⁻² for 50 cycles. Both cells exhibited the discharge plateaus of about 3.2 V and the reversible capacities of about 100 mAh g⁻¹, which is almost the same as the capacity of the cell A. It was, thus, found that the gradual decrease in discharge capacities in the solid-state cells operated under high current densities were not due to degradation of composite electrodes such as a loss of electrical contact between powders. An increase in overpotential due to the rate-limiting step of charge-transfer or mass-transfer is one possible reason.

Here, we discuss the influence of carbon conductive additives in composite positive electrodes on charge–discharge behaviors of all-solid-state cells. The cell B exhibited higher discharge plateaus and higher discharge capacities during 50 cycles than the cell C, suggesting that the overpotential observed in the cell B was lower than that in the cell C. In order to clarify the difference of cell performance, we focused on the morphologies of carbon conductive additives in composite positive electrodes where electrochemical reactions occur. AB with nano-ordered primary particles would make contact with LiCoO₂ at the nanodimensional level. However, it is difficult to homogeneously disperse AB in the composite electrodes by dry-mixing because AB is easy to aggregate by itself. On the other hand, VGCF would make contact with LiCoO₂ at multiple points along submicron-ordered fibers.

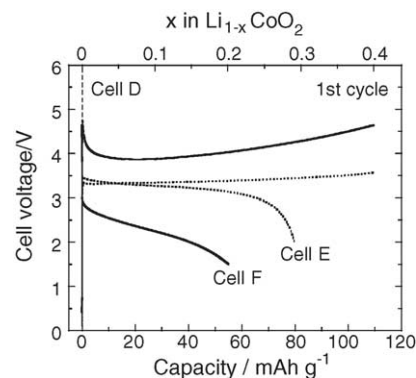


Fig. 3. First charge and discharge curves of all-solid-state In/LiCoO₂ cells without conductive additives. Detailed conditions of the cells D, E and F are described in Table 1.

Since it is easy for VGCF to form a continuous electron conducting path within an electrode, the overpotential observed under high current densities would decrease. Therefore, it is suggested that the cell B using VGCF as a conductive additive shows good cell performances even under high current densities of over 1 mA cm⁻².

In order to investigate the effect of the addition of conductive additives on cell performances, composite positive electrodes without the additives were prepared and applied to all-solid-state cells. Fig. 3 shows the first charge and discharge curves of all-solid-state In/LiCoO₂ cells without conductive additives. Dashed, solid and dotted lines denote the cells D, E and F, respectively shown in Table 1. Cell voltage of the cell D with the composite electrode (LiCoO₂:solid electrolyte = 40:60 (wt.%)) rapidly reaches 6 V in charging and the cell can not be discharged at a current density of 64 μA cm⁻². In contrast, the cells E and F with the composite electrodes (LiCoO₂:solid electrolyte = 70:30 (wt.%)) are charged and discharged. Flat charge–discharge curves and high cell voltage of about 3.3 V in discharging are obtained for the cell E, while lower cell voltage of about 2.2 V in discharging are obtained for the cell F because of a large overpotential in charging. The discharge capacities of the cells E and F are respectively about 80 and 55 mAh g⁻¹ at the first cycle. After second cycle, discharge capacities of both cells monotonically decreased with an increase in cycle number, although charge–discharge efficiencies of 100% were obtained.

Here we discuss charge–discharge behaviors of all-solid-state cells without conductive additives. LiCoO₂ shows electronic conduction by itself although it has lower electronic conductivity than carbon materials such as AB and VGCF. Not only the cell E but also the cells using the composite electrodes with 60–80 wt.% of LiCoO₂ were charged and discharged, suggesting that an electron conducting path were effectively formed in composite positive electrodes with LiCoO₂ of more than 60 wt.% and the solid electrolyte of less than 40 wt.%. The cell D was not charged and discharged because an electron conducting path in the composite electrode

was not sufficiently formed. However, the lowering of the cell voltage in discharging and the decrease in discharge capacity were observed for the cell F operating under high current densities of over 1 mA cm^{-2} . This would be also due to the overpotential in charging. It is supposed that the lithium ion and electron conducting paths formed for the cell F would not be enough to operate the solid-state cells under high current densities. Improvement on high rate performances of the solid-state cells is now in progress.

4. Conclusion

Composite positive electrodes for all-solid-state In/LiCoO₂ cells with Li₂S-P₂S₅ glass-ceramic electrolytes were prepared. In order to improve electronic conductivity of the composite positive electrodes, carbon conductive additives such as VGCF and AB were added to the composite electrodes. Under high current densities of over 1 mA cm^{-2} , the cell with VGCF exhibited better cell performances than the cell with AB, suggesting that the morphologies of conductive additives were closely related with high rate performances of all-solid-state cells. The cells using composite positive electrodes without conductive additives were also assembled and the cells with smaller amounts of LiCoO₂ were not charged and discharged even at a low current density of $64 \mu\text{A cm}^{-2}$. In the cases without conductive additives, LiCoO₂ works as not only an active material but also an electron conducting path and, therefore, increasing the amount of LiCoO₂ in the composite electrodes is needed. In fact, the cells with the electrode including LiCoO₂ of more than 60 wt.% worked as lithium secondary batteries. The formation of continuous lithium ion and electron conducting paths in the electrode is

important to enhance the cell performances of all-solid-state secondary batteries under high current densities.

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