**Preparation of Li_2S - P_2S_5 Solid Electrolyte from *N*-methylformamide solution and
Application for All-Solid-State Lithium Battery**

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Abstract

Electrode-solid electrolyte composite materials for all-solid-state lithium batteries were prepared by coating of the $\text{Li}_2\text{S-P}_2\text{S}_5$ solid electrolyte onto LiCoO_2 particles using a *N*-methylformamide (NMF) solution of $80\text{Li}_2\text{S} \cdot 20\text{P}_2\text{S}_5$ (mol %) solid electrolyte. SEM and EDX analysis showed that the $\text{Li}_2\text{S-P}_2\text{S}_5$ solid electrolyte was uniformly coated on LiCoO_2 particles. The all-solid-state cell using the LiCoO_2 particles coated with the solid electrolyte showed higher charge-discharge capacity than the cells using uncoated LiCoO_2 particles.

Keywords

All-solid-state battery, Lithium secondary battery, Sulfide solid electrolyte, Liquid phase method, Composite electrode

1. Introduction

Lithium secondary batteries have been used extensively for power sources of various portable electric devices because of their high-energy density.¹ Lithium secondary batteries have also been considered as power sources for electric vehicles and hybrid electric vehicles, which require safe batteries with high capacity. However, commercialized **lithium-ion** batteries have an obvious limitation in safety because organic liquid electrolytes have risks for leakage and flammability.

All-solid-state lithium secondary batteries with inorganic solid electrolytes (SEs) have been attracting attention for its advantages for safety and reliability.² Thus, interests of solid electrolytes with high **lithium-ion** conductivities have been increasing. Recently, Kanno et al. have reported that $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ crystals showed extremely high **lithium-ion** conductivity of over $10^{-2} \text{ S cm}^{-1}$ at room temperature.³ In addition, crystalline phases and **lithium-ion** conductivities of binary $\text{Li}_2\text{S-P}_2\text{S}_5$ systems have been studied.^{4, 5} We have reported that $\text{Li}_2\text{S-P}_2\text{S}_5$ glass-ceramics shows high **lithium-ion** conductivities of over $10^{-3} \text{ S cm}^{-1}$ at room temperature,^{6, 7} and we also have reported that all-solid-state cells with the glass-ceramics solid electrolyte worked reversibly.⁸

In addition to the development of solid electrolytes with high **lithium-ion** conductivities, formation of intimate electrode-solid electrolyte interfaces in the

bulk-type all-solid-state battery system is very important to realize high performance of all-solid-state batteries.⁹⁻¹¹ As an example, all-solid-state cells using LiCoO₂ particles coated with Li₂SiO₃ showed a high power density.¹² In order to form intimate electrode-solid electrolyte interfaces, we have reported the coating of Li₂S-P₂S₅ solid electrolyte on LiCoO₂ particles (SE-coated LiCoO₂) by the pulse laser deposition (PLD) method.^{9, 11} Charge-discharge capacities of all-solid-state cells using the SE-coated LiCoO₂ particles were higher than those of cells with uncoated LiCoO₂.

Preparation of solid electrolytes from liquid phase instead of gas-phase methods must be a very simple and effective process to form good electrode-electrolyte interfaces. Favorable solid-liquid interfaces are easily formed between electrodes and solutions of solid electrolytes, and the intimate solid-solid interfaces between electrodes and solid electrolytes can be achieved by removing solvents. Very recently, preparation of the Li_{3.25}Ge_{0.25}P_{0.75}S₄ thin film by a solution process using a hydrazine-based solvent has been reported,¹³ and we have reported that Li₂S-P₂S₅ solid electrolytes were prepared from *N*-methylformamide (NMF) solution of the 80Li₂S·20P₂S₅ (mol%) solid electrolyte.¹⁴ NMF is known to dissolve some materials containing PS₄³⁻ groups or P₂S₆ ethane-like groups,^{15, 16} and it has lower toxicity than hydrazine.

In the present study, Li₂S-P₂S₅ solid electrolyte was coated on LiCoO₂ particles by

using the NMF solution of the $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$ electrolyte to form electrode-electrolyte composite materials. All-solid-state cells using the SE-coated LiCoO_2 particles were fabricated and their battery performance was evaluated.

2. Experimental

Sulfide-based solid electrolyte was coated on LiCoO_2 particles using a *N*-methylformamide (NMF) solution of the $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$ (mol%) glass electrolyte. The $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$ glass was prepared by the mechanical milling method. Reagent-grade Li_2S (Idemitsu Kosan, 99.9%) and P_2S_5 (Aldrich, 99%) crystalline powders were used as starting materials. A mixture of these materials was mechanically milled at room temperature by a planetary ball mill apparatus (Fritsch, Pulverisette 7) using a zirconia pot (volume 45 mL) with 500 zirconia balls (4 mm in diameter). A rotating speed was 510 rpm and a milling time was 8 hours. The $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$ glass electrolyte was dissolved into NMF and a homogeneous yellow solution was prepared (Fig. 1). The concentration of the NMF solution of solid electrolyte was 10 wt%. The NMF solution was mixed with LiCoO_2 particles (D-10, Toda Kogyo Corp.) and dried at 150 °C for 3 hours under vacuum to remove NMF. The weight ratio of LiCoO_2 to dissolved SE was $\text{LiCoO}_2 : \text{SE} = 92.5 : 7.5$. The LiCoO_2 particles used in this study were coated with LiNbO_3 film in advance because all-solid-state cells using LiCoO_2 particles coated with oxides such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$,¹⁷ LiNbO_3 ¹⁸ or Li_2SiO_3 ¹² showed a high power density. All processes including the mechanical milling were performed in a dry argon atmosphere.

Temperature dependence of ionic conductivity of the powders obtained from the

NMF solution was measured by the AC impedance using an impedance analyzer (Solartron, 1260) in the frequency range of 1 Hz to 1 MHz. A pelletized sample with 10 mm in diameter and about 1 mm in thickness was used for the measurements. Carbon paste was applied to both faces of the pellet as a current collector. All measurements were performed in a dry argon atmosphere.

Morphology of LiCoO_2 particles was observed using a scanning electron microscope (SEM, JSM-6610A, JEOL) equipped with an energy dispersive X-ray spectroscopy system (EDX, JED-2300, JEOL). All-solid-state cells ($\text{In} / 80\text{Li}_2\text{S} \cdot 20\text{P}_2\text{S}_5$ glass-ceramic solid electrolyte / LiCoO_2) were constructed as follows to investigate their electrochemical performance. The $80\text{Li}_2\text{S} \cdot 20\text{P}_2\text{S}_5$ (mol%) glass-ceramic electrolyte was used as a separator layer. The $80\text{Li}_2\text{S} \cdot 20\text{P}_2\text{S}_5$ glass-ceramic electrolyte was prepared by the mechanical milling method and subsequent heat treatment.⁶ Surface coated LiCoO_2 with solid electrolytes (SE-coated LiCoO_2) and the glass-ceramic electrolyte were mixed using an mortar to prepare composite positive electrodes; the weight ratio of LiCoO_2 : SE-coatings is 92.5 : 7.5 and that of LiCoO_2 : SE (coating layer + glass-ceramic) is 70 : 30. Indium foil (Furuuchi Chem., 99.999%; 0.1 mm thickness) was used as a negative electrode. A bilayer pellet (10 mm in diameter) consisting of the composite electrode (10 mg) and the glass-ceramic electrolyte as a separator layer (80

mg) was prepared by pressing under 360 MPa, and then the indium foil was attached to the pellet by pressing under 240 MPa. The all-solid-state cells were charged and discharged using a charge–discharge measuring device (BTS-2004; Nagano Co., Ltd.) at room temperature in an Ar atmosphere.

3. Results and discussion

Figure 2 shows the temperature dependence of ionic conductivity of a pelletized solid electrolyte obtained from the NMF solution. Although the conductivity at 25°C was previously measured for the solid electrolyte,¹⁴ activation energy for conduction of the electrolyte has not been reported. Ionic conductivity of the solid electrolyte was $2.6 \times 10^{-6} \text{ S cm}^{-1}$ at room temperature. The ionic conductivity obeyed the Arrhenius law; the activation energy for the ionic conduction calculated from the slope of the plots was 42 kJ mol^{-1} . The ionic conductivity of the solid electrolyte obtained from the NMF solution was lower than that of the original $80\text{Li}_2\text{S} \cdot 20\text{P}_2\text{S}_5$ glass ($1.7 \times 10^{-4} \text{ S cm}^{-1}$),^{19, 20} and the activation energy was higher than that of original $80\text{Li}_2\text{S} \cdot 20\text{P}_2\text{S}_5$ glass (37 kJ mol^{-1}).¹⁹ The lower conductivity was caused by crystallization of Li_3PS_4 and Li_2S with low conductivity.¹⁴ Although ionic conductivity of the solid electrolyte prepared from the NMF solution was lower than that of original $80\text{Li}_2\text{S} \cdot 20\text{P}_2\text{S}_5$ glass, the conductivity was higher than that of the Li_3PS_4 crystal ($10^{-7} \text{ S cm}^{-1}$).⁵ This suggests that a glass phase with higher conductivity partially exists in the prepared electrolyte.

Figure 3 shows the SEM and EDX mapping (Co, P and S) images of the $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ solid-electrolyte-coated (SE-coated) LiCoO_2 particles. The SEM image showed that the particle size of the LiCoO_2 particles was about $20 \text{ }\mu\text{m}$; the coating materials were

observed on the LiCoO₂ particles. The particle size of LiCoO₂ was not changed by coating. Phosphorous and sulfur elements of Li₂S-P₂S₅ SE film were detected on LiCoO₂ particles, indicating that the LiCoO₂ particles were covered with Li₂S-P₂S₅ SE film. The thickness of SE on the LiCoO₂ was calculated from the surface area of LiCoO₂ (0.12 m² g⁻¹) and density of Li₃PS₄ crystals (1.872 g cm⁻³).²¹ The estimated thickness of SE layers was about 360 nm.

All-solid-state cells using the prepared SE-coated LiCoO₂ (LiCoO₂ : SE-film = 92.5 : 7.5, wt.%) or uncoated LiCoO₂ as a positive electrode material were fabricated. Figure 4 shows the initial charge-discharge curves (A) and cycle performance (B) of the all-solid-state In / LiCoO₂ cells with SE-coated LiCoO₂ (a) or uncoated LiCoO₂ (b). 80Li₂S·20P₂S₅ glass-ceramic electrolyte was added to positive electrode layers of both cells, and conductive additives such as acetylene black were not added in this study. The weight ratio of LiCoO₂ to SE including the coating layer was LiCoO₂ : SE = 70 : 30. This weight ratio was the same as that of the cell using uncoated-LiCoO₂. The cells were charged up to 3.6 V (vs. Li-In) and discharged to 2 V (vs. Li-In) at a current density of 0.13 mA cm⁻². The reversible capacity of the cells using uncoated LiCoO₂ (b) was 96 mAh g⁻¹, and that of the cell using SE-coated LiCoO₂ (a) was 107 mAh g⁻¹. These capacities were normalized by the mass of LiCoO₂ active material. The reversible

capacity of the cell (a) was higher than that of the cell (b), and cycle performance of the cell (a) was almost the same or better than that of the cell (b). Although the ionic conductivity of the solid electrolyte obtained from the NMF solution was relatively low at the present stage, the capacity of the all-solid-state cell was increased by the formation of intimate electrode-electrolyte interfaces.

The ionic conductivity of the $\text{Li}_2\text{S-P}_2\text{S}_5$ solid electrolyte obtained from the NMF solution was lower than that of the solid electrolyte prepared by the pulsed laser deposition technique.¹¹ The performance of all-solid-state cells will be improved with the increasing ionic conductivity of solid electrolytes. Future studies about electrolyte composition and solvent are needed to increase of ionic conductivities of solid electrolytes via liquid phase.

4. Conclusions

The $\text{Li}_2\text{S-P}_2\text{S}_5$ solid electrolyte was prepared from *N*-methylformamide (NMF) solution of the $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$ glass electrolyte. The ionic conductivity of the prepared electrolyte was $2.6\times 10^{-6} \text{ S cm}^{-1}$ at room temperature, and the activation energy for conduction was 42 kJ mol^{-1} . The LiCoO_2 particles were coated with the $\text{Li}_2\text{S-P}_2\text{S}_5$ solid electrolyte via the NMF solution of the glass electrolyte. The all-solid-state cell using the SE-coated LiCoO_2 particles as the electrode material showed a higher charge-discharge capacity than the cell using uncoated LiCoO_2 particles, suggesting that the intimate electrode-solid electrolyte interfaces were formed by the use of the electrolyte solution.

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Figure captions

Figure 1. *N*-methylformamide solution of the $80\text{Li}_2\text{S}\cdot 20\text{P}_2\text{S}_5$ glass electrolyte. The concentration of the solution was 10 wt%.

Figure 2. Temperature dependence of ionic conductivity of the solid electrolyte obtained from the NMF solution.

Figure 3. SEM and EDX mapping (Co, P and S) images of SE-coated LiCoO_2 particles.

Figure 4. Initial charge-discharge curves (A) and cycle performances (B) of the all-solid-state cells using SE-coated LiCoO_2 (a) and uncoated LiCoO_2 (b).

A number of lithium ion conducting glasses of oxides [4,5], sulfides [6,7], oxyhalides [8], thiohalides [9] and oxysulfides [10-13] with high performance as solid electrolytes have been prepared using a melt-quenching technique. We have prepared a series of glassy solid electrolytes of oxides [4], sulfides and oxysulfides [14] with extremely high conductivity of lithium ions by using a twin-roll casting technique [16]. However, when these glasses are used as solid electrolyte for lithium secondary batteries, the glasses should be ground into fine powders in order to make good contact with the electrode materials [17]. Mechanochemical preparation of sulfide-based glasses and glass-ceramics has also been developed from the idea that they are

Figure 1

Figure 2

Figure 3

Figure 4