Journal of Power Sources 293 (2015) 941–945

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Short communication

Preparation of high lithium-ion conducting Li_6PS_5Cl solid electrolyte from ethanol solution for all-solid-state lithium batteries

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HIGHLIGHTS

- Li_6PS_5Cl solid electrolyte was prepared from ethanol solution.
- $LiCoO_2$ was coated with Li_6PS_5Cl solid electrolyte by using the solution.
- All-solid-state batteries using the electrolyte-coated $LiCoO_2$ operated reversibly.

ARTICLE INFO

Article history:
Received 24 February 2015
Received in revised form
22 April 2015
Accepted 22 May 2015
Available online 14 June 2015

Keywords:
All-solid-state battery
Lithium secondary battery
Sulfide solid electrolyte
Liquid phase method

ABSTRACT

A Li_6PS_5Cl solid electrolyte was successfully prepared by dissolution-reprecipitation process *via* ethanol solution. An ionic conductivity of the Li_6PS_5Cl solid electrolyte from the homogeneous ethanol solution was 1.4×10^{-5} S cm^{-1} at room temperature. $LiCoO_2$ particles were coated with the Li_6PS_5Cl electrolyte *via* ethanol solution to form favorable electrode-electrolyte interface with a large contact areas. An all-solid-state cell using the electrolyte-coated $LiCoO_2$ operated as a rechargeable battery and showed the initial discharge capacity of 45 mAh g^{-1} at 25 °C.

1. Introduction

Lithium secondary batteries have been used for power sources such as electronic equipment because of their high operating voltage, high energy density and long cycle performance [1]. Recently, large-sized lithium-ion batteries are requested for application as power sources for electrical cars and stationary batteries. It is necessary for lithium-ion batteries to have higher energy density and longer cycle performance. Especially, improvement in safety of lithium secondary batteries is essential because organic liquid electrolytes used in conventional lithium secondary batteries have several risks of leakage and ignition.

All-solid-state lithium secondary batteries using inorganic solid electrolytes have been expected as next-generation batteries with higher energy density, safety and reliability [2]. In order to improve the electrochemical performances of the all-solid-state batteries, solid electrolytes with high ionic conductivities are key materials. Recently, $Li_{10}GeP_2S_{12}$ crystal has been reported to show extremely high lithium-ion conductivity of more than 10^{-2} S cm^{-1} at room temperature [3]. Crystalline phases and lithium-ion conductivities of binary $Li_2S-P_2S_5$ systems have also been studied [4,5]. We reported that $Li_2S-P_2S_5$ glass-ceramic electrolytes prepared using a mechanical milling technique exhibited a high lithium-ion conductivity of 5.2×10^{-3} S cm^{-1} at room temperature [6]. All-solid-state cells using the $Li_2S-P_2S_5$ solid electrolyte operated as secondary batteries [7].

In order to improve the electrochemical performance of the bulk-typed all-solid-state batteries, it is necessary to prepare favorable interfaces between electrodes and solid electrolytes with large contact areas [8–11]. Formation of the interfaces with the large contact areas can provide better ionic conduction path. It has been reported that all-solid state batteries using $LiCoO_2$ coated with

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http://dx.doi.org/10.1016/j.jpowsour.2015.05.093
0378-7753/

oxide solid electrolytes such as $LiNbO_3$, $Li_4Ti_5O_{12}$ and Li_2SiO_3 show a high energy density [12–14]. We have reported that $LiCoO_2$ particles were coated with $Li_2S-P_2S_5$ or Li_4GeS_4-Li_3PS_4 solid electrolyte by the pulsed laser deposition (PLD) method to prepare favorable interfaces between the electrodes and the solid electrolytes [8–10]. The all-solid-state batteries using $LiCoO_2$ coated with the solid electrolytes worked as rechargeable batteries even at large amounts of $LiCoO_2$ in the positive electrodes and showed higher capacity compared to those using non-coated $LiCoO_2$.

Preparation of the solid electrolytes by the liquid-phase method is much simpler and more effective process than the gas-phase method such as pulsed laser deposition. The favorable interfaces between solids and liquids are easily formed by using the liquid-phase method and then the preparation of the favorable interfaces between electrodes and solid electrolytes can be achieved by removing the solvents. Recently, synthesis of β-Li_3PS_4 using tetrahydrofuran (THF) has been reported as one way of preparing solid electrolytes by the liquid-phase method [15]. The ionic conductivity of the β-Li_3PS_4 electrolyte was 1.64×10^{-4} S cm^{-1} at room temperature. It has been also reported that $Li_7P_3S_{11}$ solid electrolyte, which showed the ionic conductivity of 2.7×10^{-4} S cm^{-1} at room temperature, was synthesized using 1,2-dimethoxyethane solvent [16]. These solid electrolytes had almost the same ionic conductivities at $Li_2S-P_2S_5$ solid electrolytes prepared by mechanical milling. However, in these methods, the precursors with precipitates were obtained. It is important that the precursors before drying are liquid-phase materials to prepare homogeneous electrolyte-coatings on electrodes particles with larger contact areas. Recently, we have reported that the $Li_2S-P_2S_5$ solid electrolytes were prepared using *N*-methlyformamide (NMF) solvent [17–19]. $80Li_2S \cdot 20P_2S_5$ (mol%) glass was prepared by a mechanical milling technique and then dissolved in NMF to prepare homogenous solution. Li_3PS_4 solid electrolyte was prepared from the solution by removing the solvent [17,18]. In addition, the Li_3PS_4 solid electrolyte was directly synthesized from Li_2S and P_2S_5 as the starting materials *via* homogeneous NMF solutions [19]. We have reported that the Li_3PS_4 solid electrolytes can be obtained by the process in dissolution-reprecipitation of $80Li_2S \cdot 20P_2S_5$ (mol%) glass and the process in direct synthesis from the starting materials. Moreover, we succeeded in applying the NMF solution to form favorable interfaces between electrodes and electrolytes for all-solid-state cells, and the all-solid-state cells using $LiCoO_2$ coated with the solid electrolyte operated as rechargeable batteries without the addition of solid electrolyte and carbon conductive additive particles to the positive electrodes [19]. However, the capacities of the cells were lower than those of the cells using $LiCoO_2$ coated with the solid electrolytes by PLD because the electrolytes synthesized *via* the liquid-phase showed lower ionic conductivities than those prepared by PLD. In order to improve electrochemical properties of all-solid-state batteries by coatings of solid electrolyte, it is necessary to increase their ionic conductivities.

In order to solve the issue, we have focused on electrolyte compositions and solvents. Argyrodite-type Li_6PS_5X (X = Cl, Br) crystals are attracting attention as sulfide-based solid electrolytes with a high lithium-ion conductivity [20,21]. The Li_6PS_5Cl crystal prepared by the mechanical milling technique showed a high lithium-ion conductivity of over 10^{-3} S cm^{-1} and thus it is a promising candidate of electrolytes prepared *via* a liquid-phase process. The selection of solvents is also important. Ethanol (EtOH) has much higher versatility as a solvent than NMF with a high boiling point of 199 °C. The use of EtOH with a lower boiling point should be effective in preventing side-reactions between the electrolyte coatings and electrode particles during heat-treatment for removing the solvent.

In the present report, Li_6PS_5Cl crystal was prepared by a mechanical milling technique and then dissolved in EtOH to prepare homogenous solution. The solid electrolyte was prepared from the solution by removing the solvent. The solid electrolyte was characterized by X-ray diffraction measurement and Raman spectroscopy. Ionic conductivities of the solid electrolyte were measured by AC impedance measurements. Coating of the solid electrolytes on $LiCoO_2$ particles was carried out using ethanol solution and the favorable interface between electrode and solid electrolyte with a large contact area was formed. The all-solid-state batteries using the electrolyte-coated $LiCoO_2$ particles were fabricated and characterized.

2. Experimental

A solid electrolyte Li_6PS_5Cl was synthesized using mechanical milling [20]. Li_2S (Idemitsu Kosan, 99.9%), P_2S_5 (Aldrich, 99%) and LiCl (Aldrich, 99.9%) crystalline powders as the starting materials were mixed in stoichiometric proportions. The total weight of the materials was 1 g. The mechanical milling was carried out using a planetary ball mill (Fritsch, Pulveristte 7) with a zirconia pot (45 mL in volume) and 15 zirconia balls (10 mm in diameter) at room temperature. Rotation speed was 600 rpm and the milling time was 45 h.

The synthesized Li_6PS_5Cl solid electrolyte powder was dissolved into an anhydrous ethanol (EtOH, Wako, 99.5%) solvent. After stirring for 24 h at room temperature, a homogeneous dark brown EtOH solution was obtained. The concentration of the solid electrolyte in the EtOH solution was 10 wt%. The prepared solution was dried at 80 °C under vacuum for 3 h and then powders were obtained. All the processes were performed in a dry Ar atmosphere.

Raman spectroscopies were carried out with a Raman spectrophotometer (HORIBA Jobin Yvon, Lab-Ram HR-800) to identify the structural units in the original Li_6PS_5Cl solid electrolyte, the EtOH solution and the powder prepared from the EtOH solution. X-ray diffraction (XRD) measurements were performed using an X-ray diffractometer (Rigaku, SmartLab) with a CuKα radiation to identify crystalline phases of the original Li_6PS_5Cl solid electrolyte and the powder prepared from the EtOH solution.

An ionic conductivity for the powder obtained from the EtOH solution was measured by AC impedance at room temperature using an impedance analyzer (Solartron, 1260) in the frequency range of 0.1 Hz–1 MHz. The measurements were performed for a pelletized sample with 10 mm in diameter and about 1.5 mm thick. Au thin films were coated on both faces of the pellets as current collectors. Temperature dependences of ionic conductivity were also performed. All the processes were carried out in a dry Ar atmosphere.

The prepared EtOH solution was mixed with $LiCoO_2$ particles (D-10, Toda Kogyo Corp.). The weight ratio of $LiCoO_2$ to the dissolved solid electrolyte was 92.5: 7.5. $LiCoO_2$ particles used in this study were coated with $LiNbO_3$ layer because all-solid-state cells using $LiCoO_2$ particles coated with oxides such as $LiNbO_3$, $Li_4Ti_5O_{12}$ and Li_2SiO_3 showed a high energy density [12–14]. The mixture was dried at 80 °C for 3 h under vacuum to remove EtOH solvent and then the $LiCoO_2$ particles coated with the solid electrolyte (SE-coated $LiCoO_2$) were obtained. The morphology of SE-coated $LiCoO_2$ was observed using a scanning electron microscopy (SEM, JSM-6610A, JEOL) with an energy dispersive X-ray spectroscopy system (EDX, JED-2300, JEOL).

All-solid-state cell (In/$80Li_2S \cdot 20P_2S_5$ (mol%) glass-ceramic solid electrolyte/SE-coated $LiCoO_2$) was fabricated as follows. Neither solid electrolyte particles nor carbon conductive additives were added to the positive electrode; SE-coated $LiCoO_2$ particles were only used in the positive electrodes. The $80Li_2S \cdot 20P_2S_5$ glass-ceramic for solid electrolyte was prepared by mechanical milling