



# Composite cathode prepared by argyrodite precursor solution assisted by dispersant agents for bulk-type all-solid-state batteries



Nataly Carolina Rosero-Navarro\*, Akira Miura, Kiyoharu Tadanaga

Division of Applied Chemistry, Faculty of Engineering, Hokkaido University, Sapporo, 060-8628, Japan

## HIGHLIGHTS

- $\text{Li}_6\text{PS}_5\text{Cl}$  prepared from acetonitrile/ethanol solution containing dispersant.
- $\text{Li}_6\text{PS}_5\text{Cl}$ -layer on NMC particles prepared by liquid phase process using dispersant.
- High discharge capacity of  $110 \text{ mA h g}^{-1}$  from composite cathode with 89 wt% NMC.

## ARTICLE INFO

### Keywords:

Argyrodite precursor solution  
Dispersant agents  
Low resistance interface  
All-solid-state battery

## ABSTRACT

All-solid-state lithium batteries based on sulfide solid electrolytes are potential candidates for large-scale energy storage applications. Here, composite cathode with high content of an active material was prepared by a liquid phase process assisted by a dispersant agent to produce a better electrode and electrolyte interface.  $\text{Li}_6\text{PS}_5\text{Cl}$  sulfide electrolyte derived from a solution containing dispersant showed an argyrodite crystal phase with a better distribution of particle size and higher conductivity compared with those without dispersant. Regular distribution of  $\text{Li}_6\text{PS}_5\text{Cl}$  particles in nanometric scale with a spherical shape below 500 nm and conductivity of  $0.6 \times 10^{-3} \text{ S cm}^{-1}$  ( $\rho = 1.40 \text{ g cm}^{-3}$ ) at room temperature were obtained. Composite cathode was prepared by the dispersion of  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  particles and carbon additive in the  $\text{Li}_6\text{PS}_5\text{Cl}$ -solution containing dispersant agent and subsequent drying at  $180^\circ\text{C}$ . Bulk-type all-solid-state battery fabricated with the composite cathode containing 89 wt% of the active material showed an initial discharge capacity of  $110 \text{ mA h g}^{-1}$  at  $25^\circ\text{C}$  and maintained 95% discharge capacity after 15 cycles.

## 1. Introduction

All-solid-state lithium batteries (ASLBs) are potential candidates for large-scale energy storage applications such as electrical vehicle and smart grids. The solid electrolytes (SEs) have proven to be electrochemically and thermally stable, making them suitable to be operated at high voltages and/or elevated temperatures [1]. Sulfide-based solid electrolytes (SSEs) have been widely used to fabricate bulk-type ASLBs [2–5], because of their high conductivity ( $10^{-2}$ – $10^{-4} \text{ S cm}^{-2}$ ) and sound mechanical properties (young's modulus of 20–40 GPa) [6,7]. Typically, ASLBs based on SSE are fabricated by only cold pressing, using composite cathode contains solid electrolyte and/or carbon additives to improve ionic and electronic conduction to the active material [2–5]. The amount of solid electrolyte in the composite cathode is crucial to obtain a low interfacial electrode/electrolyte resistance, however, large amount limits the total energy density. ASLBs with composite cathode prepared with a SSE amount of 30–60 wt% achieve

up to 70% of the total theoretical discharge capacity (e.g. circa of  $100 \text{ mA h g}^{-1}$  for  $\text{LiCoO}_2$  [2,3]).

Higher energy density requires the reduction of solid electrolyte content in the composite cathode. Ideally, a high content of active material of around  $\sim 90\%$  or higher, is a desired target. In this regard, an adequate distribution of each component through the composite cathode layer is the major drawback. SSE-layer deposited on active materials, such as  $\text{LiCoO}_2$  and  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  (NMC) particles, by pulsed laser deposition (PLD) [8,9] or liquid phase process [10–16] have been evaluated to produce lower interfacial electrode/electrolyte resistances. The SSE amount has been significantly reduced by PLD process. The preparation of composite cathode using  $\text{LiCoO}_2$  and rather low amount of SSE-layer around 3 wt% with a thickness of approximately 200 nm ( $\text{Li}_4\text{GeS}_4\text{-Li}_3\text{PS}_4$ ,  $1.8 \times 10^{-3} \text{ S cm}^{-1}$ ) by PLD process has recently been reported [9]. The bulk-type ASLB fabricated with this composite cathode displayed a discharge capacity of up to  $80 \text{ mA h g}^{-1}$ . The good electrochemical performance of the battery has been

\* Corresponding author.

E-mail address: [rosero@eng.hokudai.ac.jp](mailto:rosero@eng.hokudai.ac.jp) (N.C. Rosero-Navarro).

explained by the effective formation of a thin and homogenous SSE-layer on the active material particles.

The liquid phase process has also proven to be an effective and simple process to form favorable interfaces since the SSE-solution can cover the solids particles and then after solvent removal creates a SSE-layer. However, the composite cathode prepared by liquid phase process needs slightly higher SSE amount, compared with PLD process, to warrant a sufficient lithium conduction at the electrode/electrolyte interface. The preparation of composite cathodes by liquid phase process has been reported using  $\text{LiCoO}_2$  or NMC and c. a. 15 wt% SSE-layer. SSEs with high conductivity of  $10^{-4} - 10^{-5} \text{ S cm}^{-1}$  have been reported from different solvents such as methanol [12], water [13] or solvent mixture, ethanol and ethyl propionate [14]. The composite cathodes have been prepared after solvent removal at  $180^\circ\text{C} - 200^\circ\text{C}$  [12,14] or higher temperature at  $320^\circ\text{C}$  [13] to promote higher ionic conductivity of SSE-layer. Bulk-type ASLBs fabricated with these composite cathodes (15 wt% SSE) have achieved good electrochemical properties, verified by the high initial discharge capacities of  $110\text{--}120 \text{ mA h g}^{-1}$ . The effort to reduce the amount of SSE-layer ( $< 10 \text{ wt}\%$ ) into the composite cathode by liquid phase process, to increase the total energy density, inevitably leads to a drop of the discharge capacity. Initial discharge capacities between 30 and  $45 \text{ mA h g}^{-1}$  [15,16] have been reported from bulk-type ASLBs prepared with composite cathode using  $\text{LiCoO}_2$  or NMC and 7.5–10 wt%  $\text{Li}_6\text{PS}_5\text{Cl}$ -layer ( $\sim 10^{-5} \text{ S cm}^{-1}$ , precipitated from ethanol solution). The unsatisfactory electrochemical performance of these batteries can be associated with a scarce covering of SSE-coating layer on active material and/or the low conductivity of the sulfide-solid electrolytes obtained by liquid phase process. Recently, Matsuda et al. [17] satisfactorily prepared a composite cathode with a low content of SSE (10 wt%) using a  $\text{Li}_3\text{PS}_4$  nanoplates ( $2 \times 10^{-4} \text{ S cm}^{-1}$ ). The ASLB cell achieved an initial discharge capacity up to  $130 \text{ mA h g}^{-1}$ . The nanostructuring of SSE-layer could be a potential alternative to producing a better electrode/electrolyte interface, thus improving the battery performance.

The preparation of composite cathode by using liquid phase process with low content of sulfide solid electrolyte ( $< 10 \text{ wt}\%$ ) is challenging. It could be more technologically (and economically) suitable to an industrial scale-up. The aim of the present work is to prepare a composite cathode with a low content of SSE by liquid phase process, assisted by a dispersant agent. Our approach involves the strategic selection of protic/aprotic solvents and dispersant to overcome the expected drawbacks associated with the insufficient covering of SSE-layer on active material. Acetonitrile is a feasible alternative as a solvent since it has proven to play a surfactant role in the synthesis of sulfide solid electrolyte leading to the precipitation of particles in the nanometric scale and high ionic conductivity of up to  $\sim 10^{-3} \text{ S cm}^{-1}$  [18,19]. The adequate ethanol content was used to produce a complete dissolution of SSE. Moreover, a commercially available dispersant Triton X-100 was used to control the precipitation of the SSE during solvent removal and further to achieve a better electrode/electrolyte interface.

High ionic conductor solid electrolyte argyrodite-type  $\text{Li}_6\text{PS}_5\text{Cl}$  and high voltage cathode  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  were used as a reference system to prepare the composite cathode by liquid phase process as this system had been prepared by the same process using ethanol as a solvent [15,16].

## 2. Experimental

### 2.1. Synthesis of composite cathode

The  $\text{Li}_6\text{PS}_5\text{Cl}$  solid electrolyte was firstly prepared by mechanical milling process following a procedure reported previously [16]. Typically, 0.5 g of stoichiometric proportions of  $\text{Li}_2\text{S}$  (Mitsuiwa's Purity Chemicals, 99.9%),  $\text{P}_2\text{S}_5$  (Sigma Aldrich, 99%) and  $\text{LiCl}$  (Sigma Aldrich, 99.9%) were milled with 15 zirconia balls (10 mm diameter) in a

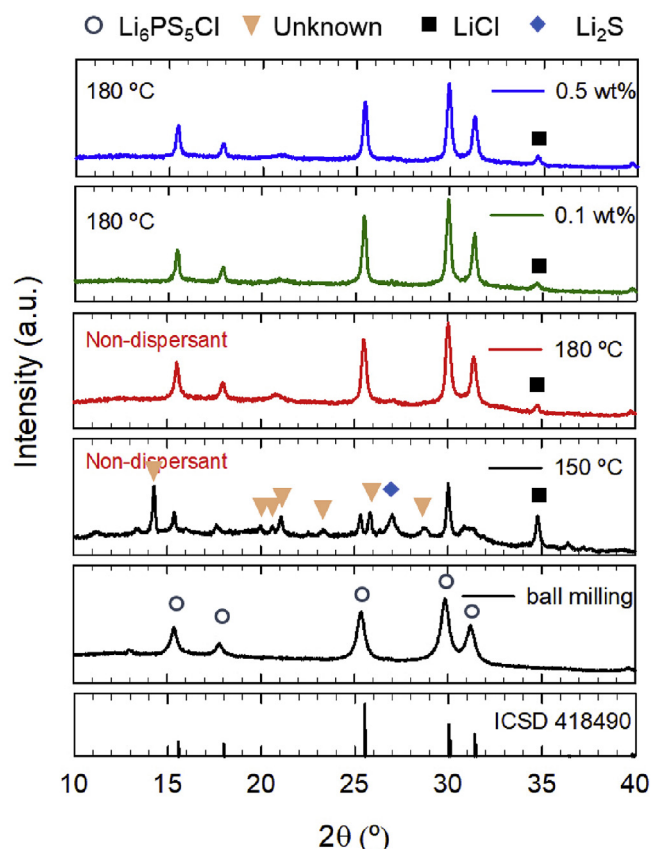


Fig. 1. XRD of the  $\text{Li}_6\text{PS}_5\text{Cl}$  obtained by mechanical milling process and after dissolution-reprecipitation process at  $150^\circ\text{C}$  and  $180^\circ\text{C}$ . XRD patterns of  $\text{Li}_6\text{PS}_5\text{Cl}$  obtained from the SSE-solution containing 0.1 wt% and 0.5 wt% of dispersant are also included.

zirconia pot (45 mL) using a planetary ball mill (PULVERISETTE, Fritsch, Germany) for 40 h at 600 RPM. The as-synthesized  $\text{Li}_6\text{PS}_5\text{Cl}$  solid electrolyte powder with an ionic conductivity of  $4 \times 10^{-5} \text{ S cm}^{-1}$  was then used to prepare the SSE-solution and further,  $\text{Li}_6\text{PS}_5\text{Cl}$ -layer on active material.  $\text{Li}_6\text{PS}_5\text{Cl}$  powder was dissolved in a mixture of ethanol (99.5%, Wako Pure Chemical, Japan) and acetonitrile (99.5%, Wako Pure Chemical, Japan), the concentration of  $\text{Li}_6\text{PS}_5\text{Cl}$  solution was  $0.1 \text{ g mL}^{-1}$ . After complete dissolution of the solid electrolyte, adequate content of triton X100 solution (dissolved in acetonitrile) was added by dropping to  $\text{Li}_6\text{PS}_5\text{Cl}$ -solution.

Crystal phase, morphology and ionic conductivity of the  $\text{Li}_6\text{PS}_5\text{Cl}$  solid electrolyte obtained by mechanical milling and dissolution-reprecipitation process were examined to elucidate the effect of the solvent and dispersants on the properties of the sulfide electrolyte. Crystal phase evaluated by X-ray diffraction (XRD) was carried out with an X-ray diffractometer (MultiFlex600, Rigaku) using  $\text{CuK}\alpha$  radiation. The ionic conductivity of pelletized samples was determined by electrochemical impedance spectroscopy (EIS) using an impedance analyser (SI 1260, Solartron) in a frequency range of 1 and  $1 \times 10^6 \text{ Hz}$  at room temperature. The solid electrolyte powders (Approximately 120 mg) were pressed under 360 MPa (at room temperature) in a polycarbonate tube, 10 mm of diameter and two stainless steel (SS) disks were used as current collectors. Morphology of the  $\text{Li}_6\text{PS}_5\text{Cl}$  solid electrolyte powders were observed by scanning electron microscopy (SEM), performed on a JIB-4600F Multibeam SEM-FIB Scanning Electron Microscope without exposure to air.

The synthesis of the composite cathodes and the assembly of the cells were conducted in a glove box under an argon atmosphere. The composite cathodes were prepared using  $\text{LiNbO}_2$ -coated  $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$  (NMC) [20,21],  $\text{Li}_6\text{PS}_5\text{Cl}$  solid electrolyte and vapor growth

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