国立大学法人 豊橋技術科学大学

TOYOHASHI UNIVERSITY OF TECHNOLOGY

PRESS RELEASE

Source: Toyohashi University of Technology, Japan, Committee for Public Relations

Release Title: Development for Novel Large-Scale Manufacturing Technology of Sulfide Solid Electrolytes

Release Subtitle: Rapid Synthesis of Highly Ion Conductive $Li_7P_3S_{11}$ Solid Electrolyte

Overview

A research group in the doctoral program of Toyohashi University of Technology's Department of Electrical and Electronic Information Engineering that includes a doctoral student Hirotada Gamo and specially appointed assistant professor Jin Nishida, specially appointed associate professor Atsushi Nagai, assistant professor Kazuhiro Hikima, professor Atsunori Matsuda and others, developed a large-scale manufacturing technology of $Li_7P_3S_{11}$ solid electrolytes for all-solid-state lithium-ion secondary batteries. This method involves the addition of an excessive amount of sulfur (S) along with Li_2S and P_2S_5, the starting materials of $Li_7P_3S_{11}$, to a solvent containing a mixture of acetonitrile (ACN), tetrahydrofuran (THF) and a slight amount of ethanol (EtOH). This helped to shorten the reaction time from 24 hours or longer to only two minutes. The final product obtained using this method is highly pure $Li_7P_3S_{11}$ without an impurity phase that showed high ionic conductivity of 1.2 mS cm^{-1} at 25 °C. These results enable us to produce a large quantity of sulfide solid electrolytes for all-solid-state batteries at low cost. The results of the research were published online by *Advanced Energy and Sustainability Research* on April 28, 2022.

Details

All-solid-state batteries are expected to be the next generation of batteries for electric vehicles (EVs) because they are very safe and enable a transition to high energy density and high output power. Sulfide solid electrolytes, which show good ionic conductivity and plasticity, have been actively developed with a view toward the applications for all-solid-state batteries in EVs. However, no large-scale manufacturing technology for sulfide solid electrolytes has been established at the level of commercialization, as sulfide solid electrolytes are unstable in the atmosphere and the process for synthesizing and processing them requires atmospheric control. For this reason, there is an urgent need to develop the liquid-phase manufacturing technology of sulfide solid electrolytes that offers low-cost and high scalability.

$Li_7P_3S_{11}$ solid electrolytes exhibit high ionic conductivity and thus are one candidate solid electrolyte for all-solid-state batteries. The liquid-phase synthesis of $Li_7P_3S_{11}$ generally occurs in an acetonitrile (ACN) reaction solvent via precursors including insoluble compounds. Conventional reaction processes like this take a long time as they go through a kinetically disadvantageous reaction from an insoluble starting material to an insoluble intermediate. Worse, it is possible that the insoluble intermediate creates nonuniformity through a complicated phase formation, leading to an increase in large-scale manufacturing costs.

Against this background, the research group worked on the development of a technology for liquid-phase production of highly ion conductive $Li_7P_3S_{11}$ solid electrolytes via uniform precursor solutions. It has been shown that the recently developed method can obtain a uniform precursor solution containing soluble lithium polysulfide (Li_2S_x) in just two minutes, by adding Li_2S and P_2S_5, the starting materials of $Li_7P_3S_{11}$, and an excessive amount of S to a solvent containing a mixture of ACN, THF and a small amount of EtOH. The key to the rapid synthesis in this method is the formation of lithium polysulfide through the addition of a small amount of EtOH or an excessive amount of S.

To elucidate the mechanism of the reaction in this method, ultraviolet-visible (UV-Vis) spectroscopy was used to investigate the chemical stability of Li_2S_x with and without the added EtOH. The study showed that the presence of EtOH made Li_2S_x more chemically stable. Thus, the reaction in this method would take the following steps. First, lithium ions are strongly coordinated with EtOH, a highly polar solvent. Next, shielding polysulfide ions against lithium ions stabilizes highly reactive $S_3^{\cdot -}$ radical anions which are a kind of polysulfide. The generated $S_3^{\cdot -}$ attacks the P_2S_5, breaking the cage structure of P_2S_5 and causing the reaction to progress. The reaction forms lithium thiophosphate which dissolves into a highly soluble mixed solvent containing ACN and THF solvents. This may have helped to obtain uniform precursor solutions very rapidly. The final product, $Li_7P_3S_{11}$, could be prepared in two hours without the necessity of ball milling or high energy treatment in the process of reaction.

The ion conductivity of the $Li_7P_3S_{11}$ obtained using this method was 1.2 mS cm^{-1} at 25 °C, higher than the $Li_7P_3S_{11}$ synthesized using the conventional liquid-phase synthesis method (0.8 mS cm^{-1}) or ball milling (1.0 mS cm^{-1}). The method proposes a new path for the synthesis of a sulfide solid electrolyte and achieves a large-scale manufacturing technology with low cost.

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Future Outlook

The research team believes that the low-cost technology for the large-scale manufacturing of sulfide solid electrolytes for all-solid-state batteries proposed in this research could be important in the commercialization of EVs equipped with all-solid-state batteries. The research focused on $Li_7P_3S_{11}$ for use as a sulfide solid electrolyte. We also want to apply this technology to the synthesis of sulfide solid electrolytes other than $Li_7P_3S_{11}$.

This research was conducted as part of the New Energy and Industrial Technology Development Organization (NEDO)'s SOLiD-EV project (JPNP 18003) aimed at the Development of Material Evaluation Techniques for Advanced and Innovative Batteries (Phase 2).

Reference

Hirotada Gamo, Jin Nishida, Atsushi Nagai, Kazuhiro Hikima and Atsunori Matsuda, T Solution Processing via Dynamic Sulfide Radical Anions for Sulfide Solid Electrolytes, *Advanced Energy and Sustainability Research*, 2022, 2200019. doi.org/10.1002/aesr.202200019

Further information

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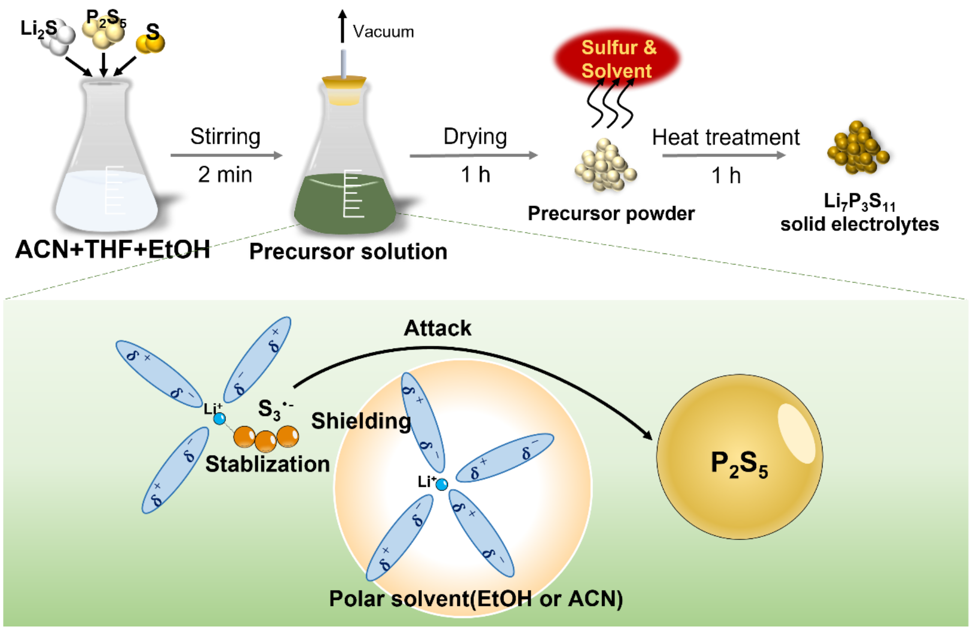
Figure1:



Title: Process enabling a reaction generating $Li_7P_3S_{11}$ using this method

Caption: The process for the liquid-phase synthesis of $Li_7P_3S_{11}$ (top) and the mechanism of the reaction (bottom) in this method

Figure2:

Title: Hirotada Gamo, doctoral student

Caption: Hirotada Gamo, a JSPS research fellow currently enrolled in a doctoral program in Toyohashi University's Department of Technology's Electrical and Electronic Information Engineering, played a central role in the research.

Keywords: Solid electrolytes, Batteries, Manufacturing, Solvents