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学位論文内容の要旨

博士の専攻分野の名称 博士 (工学) 氏名 Cecilia Marcela Calpa Ortiz

学位論文題名

Liquid-Phase Synthesis of $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ Solid Electrolytes for All-Solid-State Batteries
(全固体電池用 $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ 系固体電解質の液相合成)

The development of storage systems with high energy density is essential to enable the use of renewable energy and electric vehicles. Lithium-ion batteries are promising candidates because they offer the high energy density required. However, conventional Lithium-ion batteries possess safety issues concerns because of the use of flammable organic liquid electrolytes. All-solid-state lithium-ion batteries using inorganic solid electrolytes instead of liquid electrolytes are expected to meet the energy density and safety required.

Sulfide-based solid electrolytes are expected to be suitable solid electrolytes for the application to the all-solid-state battery because they exhibit high ionic conductivity and good mechanical properties. Recently, the synthesis of sulfide solid electrolyte by a liquid-phase process has been proposed. It is not only a more facile preparation; it also offers the possibility to control the morphology of the solid electrolytes by the solvent selection. However, the reaction mechanisms that take place during the liquid-phase synthesis have not yet been elucidated, as well the testing of the sulfide solid electrolytes prepared by liquid-phase in the all-solid-state battery is almost an unexplored area.

This thesis focused on the liquid-phase synthesis of sulfide solid electrolytes in the $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ system for the application to all-solid-state batteries. It consists of two main parts:

Part I reports the liquid-phase synthesis of $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ solid electrolytes under ultrasonic irradiation. It was found that the ultrasonic irradiation provides enough energy for the formation of PS_4^{3-} units after only 30 min. After subsequent drying at 180 °C, X-ray diffraction and Raman spectroscopy studies revealed the complex formation between PS_4^{3-} units and acetonitrile molecules. The complex between PS_4^{3-} units and acetonitrile molecules dissociated with heat treatment at 220 °C. The dissociation of the complex was accompanied by the formation of $\text{P}_2\text{S}_7^{4-}$ units resulting in the precipitation of the high ionic conductive $\text{Li}_7\text{P}_3\text{S}_{11}$ crystal phase. The synthesized $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ solid electrolyte with a Li_2S content of 74 mol%, exhibited the high ionic conductivity of $10^{-3} \text{ S cm}^{-1}$ and a small particle size below 500 nm.

For the understanding of the reaction mechanisms that take place in the liquid-phase synthesis, the Li_2S and P_2S_5 precursors and their reaction in 50:50 mol% was studied. The 50 Li_2S :50 P_2S_5 sample readily dissolved in acetonitrile to form a clear yellow solution. After subsequent drying at 180 °C

and heat treatment at 220 °C, the precipitation of the $\text{Li}_2\text{P}_2\text{S}_6$ crystal phase with local structure formed by $\text{P}_2\text{S}_6^{2-}$ units was observed. The studies on the crystallization process of the 50 Li_2S :50 P_2S_5 sample suggested that Li_2S and P_2S_5 may react in acetonitrile to form $[\text{PS}_3^-]_n$ polymeric chains with high solubility, and that the $[\text{PS}_3^-]_n$ chains may react upon heat treatment to form $\text{P}_2\text{S}_6^{2-}$ units. It is hypothesized that increase of the Li_2S content to the 50 Li_2S :50 P_2S_5 sample may break the P-S-P bonds in the $[\text{PS}_3^-]_n$ polymeric chains to form PS_4^{3-} units, that subsequently form a complex with acetonitrile molecules. Although a similar process can be expected for the formation of $\text{P}_2\text{S}_7^{4-}$ units, Raman bands corresponding to the $\text{P}_2\text{S}_7^{4-}$ units were observed only after heat treatments at temperatures above 180 °C. The possible formation mechanism of $\text{P}_2\text{S}_7^{4-}$ units may be associated with redox processes that take place at the dissociation of the complex between PS_4^{3-} units and acetonitrile molecules.

Part II reports the application of the $\text{Li}_7\text{P}_3\text{S}_{11}$ solid electrolyte prepared by liquid-phase as an ionic conductive additive in the composite cathode of all-solid-state batteries.

The electrochemical performance of an all-solid-state battery using NCM (LiNbO_3 -coated $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$) as a high voltage cathode material and the solid electrolyte containing the $\text{Li}_7\text{P}_3\text{S}_{11}$ crystal phase, prepared by liquid-phase, as the ionic conductor in the composite cathode, was investigated and compared it to that of the all-solid-state battery using a solid electrolyte containing the $\text{Li}_7\text{P}_3\text{S}_{11}$ crystal phase but prepared by mechanical milling.

The solid electrolyte prepared by liquid-phase exhibited a particle size around 500 nm, ten times smaller than the particle size of the solid electrolyte prepared by mechanical milling ($\sim 10 \mu\text{m}$). The composite cathode using the solid electrolyte obtained by the liquid-phase process displayed a better distribution of the solid electrolyte and the active material. The all-solid-state cell using NCM and the solid electrolyte prepared by liquid-phase exhibited better electrochemical performance than that using the solid electrolyte prepared by mechanical milling. The all-solid-state cells showed a first discharge capacity of 154 mAh g^{-1} and 46 mAh g^{-1} , respectively.

The local structure of the $\text{Li}_7\text{P}_3\text{S}_{11}$ solid electrolyte prepared by liquid-phase was investigated after charge-discharge measurements with high charge-end voltages (4.6 V vs. Li). Significant structural changes were not observed, indicating that the solid electrolyte containing the $\text{Li}_7\text{P}_3\text{S}_{11}$ crystal phase is stable against charge-discharge processes.

This thesis provides a new approach for the liquid-phase synthesis of sulfide solid electrolytes by using ultrasonic irradiation to enhance chemical reactivity in the solid-liquid system. Ultrasonic irradiation was demonstrated to be a useful technique to reduce the necessary time for the reaction, from days to minutes. Moreover, the liquid-process proposed in this work allowed the obtaining of sulfide solid electrolytes with high ionic conductivity and small particle size. Deeper understanding of the reaction mechanisms that take place in the liquid-phase synthesis was also provided. The advantages of the Li_2S - P_2S_5 sulfide solid electrolytes prepared by liquid-phase were demonstrated by their application to the all-solid-state battery.