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Abstract (Doctor)

Title of Thesis	Development of All-Solid-State Batteries with Sulfide Solid Electrolytes
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Approx. 800 words

This thesis reports development of all-solid-state batteries using sulfide-based lithium and sodium solid electrolytes. Rechargeable lithium-ion batteries (LIBs) have been commercially used as power sources for portable electric devices. The LIB technology has been a promise for powering electrical vehicles (EVs) in the past decade. However, in traditional LIBs, the use of organic liquid electrolytes causes some safety issues: leakage and ignition. These safety concerns hinder the market adaption for LIBs, particularly in the EVs sector. In contrast, all-solid-state Li-ion batteries (ASLBs) in which an organic liquid electrolyte is replaced by an inorganic solid electrolyte (SE) show inherently high safety. Thus, ASLBs are a viable option for their application in electric vehicles. The success of ASLBs requires large-scale manufacturing technology for sulfide SEs with high ionic conductivity. Liquid-phase processing is beneficial for achieving ASLBs manufacturing that provides high scalability and low cost. The nature of organic solvents used in the liquid-phase method determines the solubility and chemical stability of lithium thiophosphates. However, there is a lack of leading theory on the solvent effect in the liquid-phase synthesis of $\text{Li}_7\text{P}_3\text{S}_{11}$ SE, which is representative of highly conducting sulfide material. Chapter 1 constitutes general introduction. In Chapter 2, I provide guidelines for solvent selection for the liquid-phase synthesis of highly conductive crystalline $\text{Li}_7\text{P}_3\text{S}_{11}$ (Chapter 2.2) and unprecedented solution synthesis method via dynamic sulfur radical anions for the rapid and scalable manufacturing of ASLBs (Chapter 2.3). Using the developed method, the $\text{Li}_7\text{P}_3\text{S}_{11}$ SEs are prepared in a total time of 2 h through the rapid reaction of 2 min. Additionally, the $\text{Li}_7\text{P}_3\text{S}_{11}$ SEs show a higher ionic conductivity of 1.2 mS cm^{-1} at room temperature than $\text{Li}_7\text{P}_3\text{S}_{11}$ prepared by ball milling.

The improvement of energy storage devices requires not only the advances of SEs but also active materials. The active material which is conventionally used in traditional LIBs has approached its theoretical capacity limit. The restricted performance motivated the development of next-generation batteries that use active materials with high theoretical capacity. All-solid-state lithium-sulfur batteries (ASLSBs) have received much attention because of their high theoretical capacity. Nevertheless, the utilization of the high theoretical capacity of ASLSBs is limited by the

poor electronic and ionic conductivities, and sluggish redox reaction kinetics of cathode materials. In Chapter 3, I report on novel cathode materials with improved electric transport properties and their electrochemical redox behaviors. I describe the structural and electrochemical properties of $\text{Li}_2\text{S}-\text{CaS}$ in Chapter 3.2, $\text{Li}_2\text{S}-\text{CaX}_2$ ($X = \text{F}, \text{Cl}, \text{Br}, \text{and I}$) in Chapter 3.3, and $\text{Li}_2\text{S}-\text{AlI}_3$ in Chapter 3.4. Comprehensive electrochemical measurements reveal that iodide-ion that involves an oxidation reaction at a slightly higher potential than the oxidation potential of Li_2S provides desirable redox activity in ASLSBs. The implication of such redox chemistry in the additive is expanded toward understanding the role of sulfide SEs as a redox mediator and the activation mechanism in ASLSBs that is still unclear (Chapter 3.5). The electrochemistry of ASLSBs is governed by electrolyte decomposition behavior in which SEs in the cathode convert into the thiophosphates with the S-S bond in the charge/discharge process. A severe decomposition of electrolytes causes cycle fading instead of increasing the electrochemical redox activity in the early period. $\text{Li}_2\text{S}/\text{SE}$ interface modification by different rotation speeds in SE mixing allows us to control the decomposition kinetics of electrolytes.

A power system that relies on batteries using Li ions as the conducting species would be insufficient to support the growing demand for electricity because competition for lithium resources is expected to intensify in the future. All-solid-state sodium-ion batteries (ASSBs) using inorganic solid electrolytes are promising candidates for large-scale energy storage applications owing to the natural abundance and low cost of sodium sources. The commercialization of ASSBs requires the development of Na-ion SEs that show high ionic conductivity and air stability. Na_3SbS_4 prepared via a solid-phase synthetic method has attracted interest as a potential superionic conductor for ASSBs because it exhibits high conductivity ($\geq 1.0 \text{ mS cm}^{-1}$ at room temperature) and excellent air stability. In Chapter 4, I describe Cl-doped Na_3SbS_4 SEs prepared by the liquid-phase method. The specific crystal structure formed following Cl substitution enables the expansion of bottlenecks for Na^+ conduction, especially along the c-axis, which leads to the enhanced ionic conductivity of Na_3SbS_4 . Additionally, the introduction of NaCl into Na_3SbS_4 suppresses the increase in interfacial resistance that accompanies stripping/plating, thereby enhancing the cell's electrochemical stability at 0 V vs. Na/Na^+ . Overall conclusions and proposed future work are described in Chapter 5.

The findings obtained in this thesis can provide a viable path toward the development of scalable, low-cost processes for the all-solid-state battery manufacturing, an alternative material for SE and cathode materials with superior performance.