別紙４－１（課程博士（英文））

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Abstract (Doctor)

Title of Thesis	Effects of Oxide Incorporation into Sulfide Solid Electrolytes and Development of All-Solid-State Lithium-Ion Batteries.

Approx. 800 words

Solid electrolytes (SEs) play a critical role in all-solid-state lithium-ion batteries (ASSLIBs) by acting as both electron separators and ion conductors. One promising method for SE synthesis is liquid-phase synthesis, which offers scalability and energy efficiency. However, impurities and the complexity of SEs prepared through this method have posed challenges, making liquid electrolytes indispensable in many cases.

In a study aimed at addressing these challenges, highly conducting lithium-ion solid electrolytes based on a $100Li_3PS_4$-$50LiI$-xLi_3PO_4 composition ($0 \leq x \leq 20$ mol%) were successfully synthesized using liquid-phase synthesis with ethyl propionate as the reaction medium. Interestingly, the addition of Li_3PO_4 into the Li_3PS_4-LiI structure, up to x = 20, did not result in noticeable segregated peaks in the X-ray diffraction patterns.

Further analysis using 31P NMR revealed the formation of $PO_2S_2^-$ and POS_3^{3-} units, indicating that Li_3PO_4 reacted with the Li_2S-$P2S_5$ system to form Li_3PO_4-xSx. Among the synthesized electrolytes, the one with x = 10 exhibited the highest room temperature conductivity of approximately 8.5×10^{-4} Scm^{-1}.

Moreover, the study also addressed the issue of Li3PO4 impurity formation during the synthesis of Li_6PS_5Cl argyrodite SEs using liquid-phase synthesis. By replacing hydroxide-based solvents with thiol-based solvents, Li_3PO_4 was successfully eliminated from the Li_6PS_5Cl SEs. This modification resulted in the Li_6PS_5Cl SEs achieving the highest ionic conductivity value (>2 $mS \cdot cm^{-1}$) ever reported through liquid-phase synthesis. Importantly, the absence of Li_3PO_4 in the argyrodite SE led to significantly increased capacity and remarkable stability.

To further enhance the stability of the Li_6PS_5Cl argyrodite SE, the study explored oxygen doping by synthesizing $Li_6PS_{5-2.5x}O_{2.5x}Cl$ (x = 0, 0.05, and 0.10) solid electrolytes using liquid-phase synthesis. The solid electrolyte with x = 0.05 exhibited high ionic conductivity along with improved electrochemical stability against lithium metal and oxide cathodes. Argyrodites with x = 0.05 and x = 0.10 demonstrated superior capacity retention and higher Coulomb efficiency compared to x = 0. Moreover, the solid electrolytes exhibited enhanced stability during Li symmetrical cell measurements.

Overall, this work provides valuable insights into achieving high-performance ASSLIBs through liquid-phase synthesis. By carefully controlling the composition and synthesis conditions, such as introducing Li_3PO_4 or oxygen doping, it is possible to optimize the conductivity and stability of the solid electrolyte systems, paving the way for the development of advanced all-solid-state lithium-ion batteries.

In addition to addressing stability challenges in sulfide-based solid electrolytes, oxygen substitution offers several notable advantages for the performance and functionality of these materials in ASSLIBs.

The incorporation of Li_3PO_4 into the Li_3PS_4-LiI system and P_2O_5 into Li_6PS_5Cl lead to the formation of oxysulfide units. These oxysulfide compounds play a crucial role in enhancing the electrochemical stability of the solid electrolyte, particularly at the interface. The presence of the oxysulfide units helps to minimize unwanted reactions and side effects, improving the overall stability and performance of the solid electrolyte. This finding highlights the potential of incorporating Li_3PO_4 and P_2O_5 as strategies to enhance the electrochemical stability of solid electrolytes, making them promising candidates for advanced energy storage applications.

In summary, oxygen substitution in sulfide-based solid electrolytes provides numerous benefits for all-solid-state lithium-ion batteries. It enhances Li-ion conductivity, improves electrochemical stability, expands the electrochemical window, promotes compatibility with oxide cathodes, and allows for precise control over doping levels. These advantages contribute to the development of high-performance ASSLIBs with improved energy storage capacity, longer cycle life, and enhanced overall battery performance.