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Author(s)	Fang, Tong
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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　FANG Tong

学 位 論 文 題 名

Development of Sulfide-based Inorganic-Organic Hybrid Solid Electrolytes for All-solid-state Lithium Batteries
（全固体リチウム電池用硫化物系無機・有機ハイブリッド固体電解質の開発）

All-solid-state lithium batteries have gained significant attention due to their high safety and energy density, particularly for use in electric vehicles and portable electronic devices. However, commercialization faces challenges such as electrolyte ionic conductivity, interfacial stability, and manufacturing cost. Sulfide solid electrolytes are a key focus due to their high ionic conductivity and excellent interfacial compatibility, but their environmental sensitivity and mechanical properties that still need improvement limit their practical applications.

In this study, a novel sulfide-based inorganic-organic hybrid electrolyte was developed by introducing organic cations to improve mechanical flexibility and accommodate volume changes of silicon electrodes, thereby enhancing cycling stability and safety.

Chapter 1 provides a detailed introduction to the development background, current research status, and technical challenges faced by all-solid-state lithium batteries.

Chapter 2 details the preparation and characterization methods of the materials used in the experiments. Inorganic-organic hybrid sulfide solid electrolytes containing different organic cations (such as tetramethylammonium iodide (TMAI), tetraethylammonium iodide (TEAI), tripropylammonium iodide (TPAI), and tetrabutylammonium iodide (TBAI)) were prepared by ball milling. The samples were comprehensively characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), and electrochemical impedance spectroscopy (EIS), and their thermal stability and mechanical properties were explored.

Chapter 3 describes the preparation and evaluation of (1-x) $Li_7P_2S_8I$ · x TMAI (x = 0, 0.05, 0.1, 0.2)

inorganic-organic hybrid electrolytes. With an increase in the TMAI doping amount, the total ionic conductivity slightly decreases but the bulk conductivity increases, indicating that TMAI doping can promote lithium ion migration. In addition, the doped samples exhibited stable lithium plating/stripping performance in lithium symmetric cells, demonstrating good interfacial stability between the doped electrolyte and lithium metal.

In Chapter 4, the effects of four tetraalkylammonium iodides (TMAI, TEAI, TPAI, TBAI) on the structure and electrochemical performance of $Li_7P_2S_8I$-based electrolytes were examined. The results showed that both the undoped sample and all doped samples maintained an amorphous structure, indicating that the introduction of tetraalkylammonium iodides did not alter the structural characteristics of the material, thereby ensuring consistency in material performance. The crystallization temperature of the obtained materials slightly decreased with an increase in the doping amount, showing that the dopant cations are homogenously distributed in the amorphous matrix. Furthermore, with an increase in the carbon chain length of tetraalkylammonium and doping concentration, the ionic conductivity of the electrolyte generally decreases, especially showing complex nonlinear behavior in the TBAI series.

In Chapter 5, all-solid-state lithium batteries were assembled using the newly developed inorganic-organic hybrid sulfide electrolyte, and their cycling performance was evaluated. The electrolyte doped with TMAI significantly improved the cycling stability of the battery. The cell with 0.2 TMAI-doped $Li_7P_2S_8I$ maintained a discharge capacity of 2014 mAh g^{-1} after 10 cycles without significant decay. This improvement is mainly attributed to the increased flexibility of the electrolyte, which effectively mitigated the volume changes of the silicon electrode and prevented electrode cracking.

Chapter 6 evaluates the mechanical properties of the hybrid electrolytes. Different types of tetraalkylammonium iodide doping altered the mechanical properties of the sulfide electrolytes. The sample doped with TEAI exhibited the highest elastic modulus (25.2 GPa), while the TBAI-doped sample had the lowest elastic modulus (18.4 GPa), which is related to the molecular structure of the dopant. The longer chain structure of TBAI may have increased the free volume of the material.

In summary, this study investigated the effects of tetraalkylammonium iodide doping on the mechanical and electrochemical properties of sulfide-based solid electrolytes. The results indicate that these materials have potential applications in all-solid-state lithium batteries. These findings provide some preliminary insights for developing high-performance all-solid-state batteries and contribute to the further development of future energy storage technologies.