

Development of High-Performance NASICON-Type Electrolytes and Their Implementation in All-Solid-State Sodium-Ion Batteries

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論 文 名 : Development of High-Performance NASICON-Type Electrolytes and Their Implementation in All-Solid-State Sodium-Ion Batteries
(高性能 NASICON 型電解質の開発と全固体ナトリウムイオン電池への展開)

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論 文 内 容 の 要 旨

All-solid-state batteries (ASSBs) offer significant advantages over conventional lithium-ion batteries, particularly in terms of safety and durability, as they eliminate combustible organic electrolytes. Recently commercialized oxide-based Li^+ -ion ASSBs, with a monolithic laminated structure similar to that of multi-layer ceramic capacitors (MLCCs), broaden the scope of applications in energy storage systems, especially in their practical implementations within electronic devices. The general objective of this work is to develop oxide-based Na^+ -ion ASSBs. A review of the current state of oxide-based Na^+ -ion ASSBs reveals several challenges: (1) insufficient ionic conductivity or the need for high sintering temperatures in oxide ceramic electrolytes, (2) difficulties in co-sintering the electrolyte and electrodes, along with associated interfacial issues, (3) a lack of high-capacity, low-potential anode materials, and (4) significant volume changes in the electrode active materials. This thesis shoots for these challenges, aiming to develop high-performance electrolytes, anode, and cathode materials for oxide-based Na^+ -ion ASSBs. Specifically, the focus is on NASICON-type electrolytes and electrodes for the construction of these batteries. The significance of NASICON-type materials lies not only in the high performance potential of the electrodes and electrolytes but also in the compatibility of the electrode-electrolyte structure, which promotes the formation of stable interfaces.

Chapter 1 presents the background and objectives of this study.

In Chapter 2, we develop an $\text{Na}_3\text{Zr}_2(\text{SiO}_4)_2(\text{PO}_4)$ -based electrolyte, achieving a remarkable conductivity of $6.0 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature, rivaling that of sulfide-based electrolytes. This is accomplished by optimizing the composition in the range $\text{Na}_{3+x+y}\text{Zr}_{2-y}\text{Al}_y\text{Si}_{2+x}\text{P}_{1-x}\text{O}_{12}$ ($0.10 \leq x \leq 0.50$, $0 \leq y \leq 0.1$) sintered at 1270°C . Despite the issue of reduced sinterability with increasing Si/P ratio due to the formation of a viscous SiO_2 -rich grain boundary interphase, the addition of Al_2O_3 effectively reduces the viscosity and improves the sinterability. In other words, a strategy of engineering the liquid phase that is *in-situ* generated from the host phase is viable. The enhanced conductivity is attributed not only to the lowered grain boundary resistivity but also to lattice expansion from modified Na occupations in the crystal structure. Furthermore, this material demonstrates a wide electrochemical window, suppressed partial electronic conductivity, low polarization voltage in direct contact with a Na anode, and stable charge-discharge cycles with a direct junction to

glass-ceramic derived $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ cathode.

In Chapter 3, since the high sintering temperature of 1270 °C is not ideal for co-sintering with electrode materials, we introduce the mixture of B_2O_3 and Na_2CO_3 to lower the sintering temperature of the electrolytes. This successfully reduces the sintering temperature to 900 °C, while preserving its high ionic conductivity. The total ionic conductivity fantastically achieves an impressive $4.5 \times 10^{-3} \text{ S cm}^{-1}$ in $\text{Na}_{3.4}\text{Zr}_{1.95}\text{Al}_{0.05}\text{Si}_{2.35}\text{P}_{0.65}\text{O}_{12}$ -10%wt(Na_2CO_3 - B_2O_3) at room temperature. Furthermore,, the solid-state electrolyte sintered at 900 °C exhibits a wide electrochemical window $> 5 \text{ V}$, a low electronic conductivity $< 10^{-9} \text{ S cm}^{-1}$, and good compatibility with Na metal anode.

In Chapter 4, hard carbon is identified as a promising option for the negative electrode in Na-ion batteries due to its high capacity and low potential. While organic liquid electrolyte systems have been extensively investigated, their application in sintering processes has not been thoroughly explored, likely due to the challenging reactivity between oxide and carbon materials. This study successfully integrates hard carbon spheres (HCS) into $\text{Na}_{3.4}\text{Zr}_{1.95}\text{Al}_{0.05}\text{Si}_{2.35}\text{P}_{0.65}\text{O}_{12}$ -10%wt($2\text{Na}_2\text{CO}_3$ - B_2O_3) (NZAS_{2.35}P-10N₂B) electrolyte to construct a composite electrode (HCS+NZAS_{2.35}P-10N₂B) through atmospheric pressure sintering at 900 °C. This composite electrode demonstrates good electrochemical performance at room temperature without the need for organic or liquid additives.

In Chapter 5, an all-solid-state Na^+ -ion battery consisting of HCS+NZAS_{2.35}P-10N₂B | NZAS_{2.35}P-10N₂B | $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ was fabricated through pressureless sintering. The battery operates at room temperature and delivers an initial discharge capacity of over 60 mAh g⁻¹ with a voltage cut-off between 1.5 V and 4.0 V. However, the battery suffers from capacity fading over cycles. To address this issue, an electrochemical presodiation technique was applied.

In Chapter 6, the phase and volume changes of the glass-ceramic-derived $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ electrode during the charge-discharge process in an all-solid-state system were investigated in detail. The effects of highly conductive carbon nanotubes on the compatibility with the sintering process of the glass-ceramic-derived $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ electrode, as well as their role in enhancing battery performance, were thoroughly examined. A glass-ceramic-derived $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ symmetric battery with an NZSP-based electrolyte, free from organic conductive additives, was successfully fabricated. The battery exhibits a capacity greater than 80 mAh g⁻¹ and demonstrates high cycle durability at room temperature.

In Chapter 7, the research on all-solid-state Na^+ -ion batteries was extended to all-solid-state Na-air batteries. Composite air electrodes, combining NASICON electrodes with carbon nanotubes, were developed. These composite electrodes were sintered onto the surface of an NZSP-based ceramic electrolyte. The charge-discharge curves of the all-solid-state Na | NZSP-based electrolyte | composite air electrode batteries in air were examined at room temperature.

Chapter 8 provides overall conclusions and outlooks of this study.