

Glass-Ceramic Processes of NASICON-Type $\text{Na}_3\text{M}_2(\text{PO}_4)_3$ (M= Ti, V) for All-Solid-State Sodium-Ion Batteries

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論 文 名 : Glass-Ceramic Processes of NASICON-Type $\text{Na}_3\text{M}_2(\text{PO}_4)_3$ ($M = \text{Ti}, \text{V}$) for All-Solid-State Sodium-Ion Batteries
(全固体 Na イオン電池に向けたナシコン型 $\text{Na}_3\text{M}_2(\text{PO}_4)_3$ ($M = \text{Ti}, \text{V}$) のガラスセラミックプロセス)

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論 文 内 容 の 要 旨

All-solid-state batteries (ASSBs) have attracted increasing attentions due to their predominance in safety and durability by eliminating combustible or degradable organic components. Recently commercialized oxide-based ASSBs in Li-system has a monolithic laminated structure similar to multi-layer ceramic capacitors (MLCCs), and are practically implemented to electronic devices. Here, several issues need to be addressed for enhancing their performances and reducing their costs, including exploration of high-performance materials for an electrode, an electrolyte and other components, compatibility and co-sintering of these materials, substitution of precious constituent elements. Then this study addresses NASICON-type Na^+ ion conducting and/or insertion materials. We also consider compatibility of NASICON materials to glass-ceramic method, which is beneficial to not only a facile synthesis of powder or bulk materials, but also the lowering the sintering temperature for the fabrication of oxide-based ASSBs. A structure of ASSBs is also focused on; the laminate layer thickness is currently on the order of several tens of micrometers. To meet a demand of thinner thickness in the future, this study explores spin coating technique. In this thesis, we investigate the glass-ceramic NASICON-type $\text{Na}_3\text{M}_2(\text{PO}_4)_3$ ($M = \text{Ti}, \text{V}$) electrode materials in detail in terms of crystallization behavior in different atmosphere, and electrochemical performance in both organic liquid electrolyte and all-solid-state batteries. The organization of the thesis is as follows.

Chapter 1 is dedicated to share the background and the purpose of this study.

In Chapter 2, NASICON-type $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (NVP) was prepared via a crystallization from $37.5\text{Na}_2\text{O}-25\text{V}_2\text{O}_5-37.5\text{P}_2\text{O}_5$ (mol%) glass. The crystallization behavior of $37.5\text{Na}_2\text{O}-25\text{V}_2\text{O}_5-37.5\text{P}_2\text{O}_5$ (mol%) glass with the composition equivalent to that of NVP was explored in detail by a combination of XRD and TG-DTA at different conditions (atmosphere: N_2 or 5% H_2/Ar , glucose: with or without). The electrochemical performances of NVP glass-ceramics were measured. Typically, a reducing atmosphere of 5% H_2/Ar is inadequate to obtain a full transition of NVP. Glucose as a reducing agent and an effective source for carbon conductive aid during glass-ceramic process was demonstrated to be crucial for not only suppressing the formation of NaVP_2O_7 and but also decreasing the crystallization temperature of NVP ($> \sim 600$ °C) in both N_2 and 5% H_2/Ar atmosphere compared to that in 5% H_2/Ar atmosphere (~ 700 °C). From the view of full conversion of NVP, the crystallization of glass with 10 wt.% initial glucose addition in 5%

H₂/Ar atmosphere performs best. The formation of NVP is associated with a loss of excess oxygens in the initial glass composition and a reduction of V from V⁵⁺ and V⁴⁺ to V³⁺. The electrochemical properties of NVP glass-ceramics as a cathode have been investigated and demonstrated a good electrochemical capacity 115 mAh g⁻¹ that is comparable to the theoretical value.

In Chapter 3, glass-ceramic processes have been investigated to prepare NASICON-type Na_xTi₂(PO₄)₃ (NTP) from 30Na₂O–40TiO₂–30P₂O₅ glass with varied atmospheric conditions (N₂ or 5 % H₂/Ar) and varied temperatures (550–850 °C). The electrochemical performances of NTP glass-ceramics were measured. Typically, by annealing in the inert (N₂) atmosphere, the glass started crystallizing into NASICON-type NaTi₂(PO₄)₃ (N1TP) with rhombohedral symmetry at ~600 °C followed by crystallization of other phases to be multiphase mixtures at higher temperatures. In contrast, in the reducing (5% H₂/Ar) atmosphere, NASICON-type Na₃Ti₂(PO₄)₃ (N3TP) with triclinic symmetry is crystallized at >~800 °C. The formation of N3TP is associated with a loss of excess oxygens in the initial glass composition and a reduction of Ti from Ti⁴⁺ to Ti³⁺. The reduction process upon the glass-to-ceramic conversion was traced by in-situ observation during the thermogravimetric analysis. It is also revealed that the electrochemical Na⁺-storage capabilities of the glass-ceramic electrodes are correlated with the Na-ion occupancy between these two phases, and their phase fractions affect the charge-discharge properties of Na-ion cells. Finer glass-ceramic powders could improve the electrochemical properties and achieve almost 80 % of its theoretical capacity.

In chapter 4, NTP electrode film with 1 μm-scale thickness on Na₃Zr₂(SiO₄)₂(PO₄) (NZSP) electrolyte pellet was prepared via a combination of spin coating and glass-ceramic method. The stable coexistence of NTP and NZSP during glass-ceramic by XRD, the tight interface junction of NTP–NZSP were explored. The impacts of an electrode active material with 1 μm-scale thickness on performance of oxide-based all-solid-state battery (ASSB) have been investigated by metallic Na | NZSP | Na₃Ti₂(PO₄)₃ (NTP) cells. Typically, dense crystalline NTP layer is formed on NZSP ceramic electrolyte using spin coating of glass powder suspension and subsequent crystallization (glass-ceramic process). A sample with 0.6 μm thick NTP layer exhibits 0.1C charge/discharge cycling with very small polarization (< 0.03 V), and its initial capacity of ~60 mAh g⁻¹ is retained > 80% after 60 cycles. Fast cathode kinetics also realized the 0.1C capacity at –20 °C to be ~80% retention. Furthermore, a facile control over the thickness of cathode films without any conductive additives in the 1 μm range demonstrated in this work enables the assessment of cathode kinetics. Electrochemical impedance spectroscopy revealed Warburg resistance originates from an ambipolar diffusion of electron and Na⁺ ion. The methodology presented here paves a way for rapid examinations of electrode material compatibility and electrode design for next-generation oxide-based ASSBs.

Chapter 6 gives overall conclusions of this study.

In summary, this study provides key knowledge and technologies for production of next-generation secondary-batteries, and contribute to development in disciplines of physical chemistry of solids and ceramic engineering.