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Improving ionic conductivity of Nasicon ($Na_3Zr_2Si_2PO_{12}$) at intermediate temperatures by modifying phase transition behavior

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HIGHLIGHTS

- Na^+ ion conductivity at intermediate temperatures improves by adding Ge to Nasicon.
- Reduction of the phase transition temperature by adding Ge has been verified.
- Modifying phase transition behavior can enhance Na^+ ion conductivity of Nasicon.

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ABSTRACT

Molten sodium (Na) anode high temperature batteries, such as Na-$NiCl_2$ and Na-S, draw attentions to be used in stationary electricity storage applications. Recent efforts are exerted to lower their operating temperatures down to below 200 °C in order to adopt ultra-low cost cell production, establish easier maintenance, pursue enhanced safety, and more. One of main challenges in lowering the operation temperature is radical decrease in ionic conductivity of their solid electrolytes. $Na_3Zr_2Si_2PO_{12}$ (Nasicon) is considered as a solid electrolyte for the lower temperature operation. Here we report Na ionic conductivity of Nasicon at 150 °C increases by adding Ge element. The ionic conductivity of Ge-added sample ($Na_3[Zr_{2-\delta}Ge_\delta]Si_2PO_{12}$, $\delta = 0.1, 0.2$) is measured as high as 1.4×10^{-2} S cm^{-1} at 150 °C which is about two times higher than those of the bare Nasicon. The phase transition temperature of the Ge-added samples is lowered, thereby the volume fraction of the rhombohedral phase, which is stable at higher temperatures and exhibits higher Na ion conductivities, increases. This finding provides a useful guideline to further increase the ionic conductivity of Nasicon solid electrolytes, which can advance materialization of lower temperature operating Na batteries.

1. Introduction

Advanced molten sodium (Na) anode high temperature batteries such as Na-S and Na-$NiCl_2$ are attractive for use in large scale energy storage because of a number of advantages, such as use of inexpensive materials, demonstrated long lifetime, and easiness to be scaled up [1–7]. Therefore, the technologies have been successfully demonstrated for stationary applications [4,8]. Operating these batteries at elevated temperatures of 280–350 °C enables their active materials (Na, S, and $NaAlCl_4$) to remain in a molten state; however, the high temperature operation is one of the major drawbacks of the conventional Na-based batteries which causes increased component degradation kinetics, higher manufacturing cost, and loss in energy efficiency [9–11]. Therefore, intensive efforts on this technology have been focused on developing advanced batteries that can be operated at intermediate temperatures (95–190 °C) [9–11] or even at room temperature [12–16].

For such advanced lower temperature operating Na batteries, development of suitable solid electrolytes with high ionic conductivity is essential because Na-ion conductivity of a solid electrolyte at lower temperatures is typically 1 to 2 orders of magnitude lower than that at high temperatures of above 300 °C [2,17,18]. Among candidate solid electrolytes, Nasicon, $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ ($0 \leq x \leq 3$), has been attracted due to its high ionic conductivity especially at $x = 2$ ($Na_3Zr_2Si_2PO_{12}$) [19–21] that is comparable to that of β”-Al_2O_3, which has the highest ionic conductivity among Na^+ superionic conductors and it could be even higher at low temperature regime [17,18].

Nasicon is a solid solution of $NaZr_2P_3O_{12}$ and $Na_4Zr_2Si_3O_{12}$ and is composed of corner-shared ZrO_6 and $(P/Si)O_4$ polyhedral framework

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that forms three dimensional Na^+-conducting channels. Nasicon compounds ($Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$, $0 \leq x \leq 3$) have a rhombohedral phase ($R\bar{3}c$), but a monoclinic phase (C2/c) can be stabilized at specific compositions ($1.6 \leq x \leq 2.4$) and temperature conditions ($< \sim 150$ °C) [20,22,23].

The phase transition (monoclinic ↔ rhombohedral phase) of Nasicon ($Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$, $1.6 \leq x \leq 2.4$) can happen at certain temperatures [24]; during this transition, the configuration of Na^+ ions is slightly changed remaining ZrO_6 and $(P/Si)O_4$ polyhedral frameworks [20]. Rhombohedral Nasicon structure has four equivalent Na sites (one Na_1 and three Na_2) per formula unit, and the three Na_2 sites split into one Na_2 and two Na_3 sites as it transforms to monoclinic phase. In rhombohedral phase, only Na_1 site is fully occupied whereas the Na_1 and Na_2 sites are fully occupied in monoclinic phase. This rearrangement can affect the conducting pathway of Na^+, and it also causes the slight distortion of the structure.

Furthermore, the phase transition behavior strongly affects the transport of Na^+ because the rhombohedral phase is more symmetric than the monoclinic phase and thereby has higher Na^+ ion mobility [25,26]. Therefore, the rhombohedral phase that is stable at high temperature has lower activation energy (E_a) than the monoclinic phase. Stabilizing the rhombohedral phase at lower temperatures can increase the ionic conductivity (σ_{ion}). Considering that typical approaches to improve the ionic conductivity are to enhance sinterability or to enlarge conduction channels by doping various dopants into Zr octahedral sites [17,27–31], stabilizing rhombohedral phase at low temperature can be alternative approach to increase σ_{ion} in Nasicon compounds. Excess sodium in the compound, e.g., $Na_{3.3}Zr_2Si_2PO_{12}$ compared with $Na_3Zr_2Si_2PO_{12}$, can increase the ionic conductivity as well [32]. Since the operating temperature of the advanced Na batteries operated at intermediate temperatures overlaps the transition temperature of Nasicon, understanding phase transition behavior would be critical which can broaden their applications as a promising solid electrolyte.

In this study, $Na_3Zr_2Si_2PO_{12}$ was synthesized with and without Ge to understand the phase transition behavior of Nasicon and the effect of the phase transition on the electrical properties. The effects of Ge addition to Nasicon having a baseline composition ($Na_3Zr_2Si_2PO_{12}$) on its phase transition behavior and ionic conductivity were investigated by using high-temperature *in-situ* synchrotron X-ray diffraction (*in-situ* XRD), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FT-IR), Differential Scanning Calorimeter (DSC), and AC impedance spectroscopy. As the amount of Ge addition increased, the phase transition temperature (T_P) was lowered and the content of rhombohedral phase compared to monoclinic phase at the transition temperature range was increased. The improvement of σ_{ion} can be the result of the increase in the contents of the rhombohedral phase that can increase Na^+ ion mobility. The findings in this study can provide an alternative way to the increase in ionic conductivity in Nasicon compounds and to apply Nasicon to Na batteries that can operate at intermediate temperature.

2. Experimental section

2.1. Sample preparation

The Nasicon ("bare sample", $Na_3Zr_2Si_2PO_{12}$ stoichiometry) and Ge-added Nasicon ("Ge-added sample", $Na_3Zr_{2-\delta}Ge_\delta Si_2PO_{12}$ where $\delta = 0.1$, 0.2 stoichiometry) were synthesized by solid-state reaction. The bare sample was prepared by mixing stoichiometric amounts of Na_2CO_3, ZrO_2, SiO_2, and $NH_4H_2PO_4$. To prepare the Ge-added samples, a part of ZrO_2 precursor was replaced by GeO_2. Details of sample preparation process are shown in our previous study [32]. The Zr-deficient Nasicon ("Zr-deficient sample", $Na_3Zr_{2-\delta}Si_2PO_{12}$ where $\delta = 0$, 0.1, 0.2 stoichiometry) were also prepared to confirm effects of adding Ge element on final products, and experimental results of the Zr-deficient samples is included in Supplementary materials (see Fig. S1, Fig. S6, Table S1 and Table S2).

2.2. Material characterizations

The crystal structure of the samples was characterized using synchrotron powder X-ray diffraction (XRD) at the 9B High Resolution Powder Diffraction beamline of the Pohang Light Source II (PLS-II), Korea. Synchrotron XRD of the samples was recorded with six base detectors using a step size of 0.02°, exposure time of 6 s, and $10 \leq 2\theta \leq 130°$ at room temperature (RT). *In-situ* synchrotron XRD patterns at high temperature (above 100 °C) were taken with a step size of 0.01°, exposure time of 2 s, and $10 \leq 2\theta \leq 130°$ at $100 \leq T \leq 130$ °C. XRD patterns were analyzed with X'pert highscore plus software program using Rietveld refinement. The morphology of the sintered pellets was observed using a BV field emission scanning electron microscopy (SEM, XL30S FEG, Philips Electron Optics) at a vacuum level of below 10^{-5} mbar with accelerating voltage of 5 kV. The binding energy of Ge element in the Nasicon samples was studied using an X-ray photoelectron spectroscopy (XPS) with VG scientific XPS equipment (VF ESCALAB 350). Core level energies were calibrated using the C-C bonding in C 1s (284.6 eV). FT-IR spectra of the samples in 400–1300 cm^{-1} range were obtained with the use of a Nicolet iS50 FT-IR Spectrometer. The FT-IR spectra of the samples were taken on Nasicon powder samples. DSC on the Nasicon samples was performed using a SDT Q600 (TA instruments) at $25 \leq T \leq 300$ °C with a flow of synthetic air (50 ml/min). Ramping rate was 10 °C/min in all experiments.

2.3. Electrical property measurement

Pt blocking electrodes (thickness ~ 100 nm) were deposited on both sides of pellets by sputtering. AC impedance spectroscopy was performed in the frequency (f) range $1\text{ Hz} \leq f \leq 1\text{ MHz}$ at $100\text{ °C} \leq T \leq 300\text{ °C}$ in air. The bulk impedance was obtained from the intercept of the Nyquist plot with the real axis at high f. σ_{ion} was calculated using the impedance and area and thickness of the pellets.

3. Results

3.1. Material characterizations

The synchrotron XRD patterns (Fig. 1a) of the bare sample and the Ge-added samples show that all samples have the monoclinic Nasicon phase with certain amount of monoclinic ZrO_2 as a secondary phase (blue inverted triangle in Fig. 1a) and without any Ge-related phases. The results of Rietveld refinement of the samples are included in Supplementary materials (see Fig. S1, and Table S1). The ZrO_2 impurity can be formed by loss of Na and P at high temperature during the solid-state reaction [26,27,33,34] or due to the low reactivity of monoclinic ZrO_2 [27]. Lattice parameters of the three samples were obtained by XRD refinement (Fig. 1b), and those of the bare sample are similar to values reported in the literature [35]. However, lattice parameters in the Ge-added samples were a little larger than those in the bare sample and linearly increased according to the Ge amount. As observed in reported $NaGe_2(PO_4)_3$ compound, Ge^{4+} ions can occupy octahedral sites of Nasicon lattice instead of Zr [36,37]. However, given that the Ge^{4+} ion have much smaller ionic radius (~0.53 nm) than Zr^{4+} ion (~0.72 nm) and lattice parameters of the Ge-added samples are increased, added Ge barely goes to the Zr site in the bulk structure. To understand the effect of Zr deficiency on lattice parameters of the Ge-added samples, the Zr-deficient samples were additionally synthesized based on the amount of Zr element and then its lattice parameters were compared to those of the Ge-added samples (Fig. 1b). Lattice parameters of the Zr-deficient samples almost kept constant values whereas those values of the Ge-added samples linearly increased according to the Ge amount. This