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Single-phase All-solid-state Batteries using NASICON-type Oxide Materials

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Abstract: *All-sold-state batteries have been expected as the next-generation secondary battery due to its high reliability and safety. However, the difficulty for the commercialization is the interfacial resistance between electrode and electrolyte which is larger than the bulk ionic conductivity of the electrolyte. "Single-phase all-solid-state batteries" are adopted as a new concept in order to reduce the interface resistance between the electrodes and the electrolyte, compared to the conventional all-solid-state batteries which have clearly several components (i.e. electrolyte part and electrode parts). Single-phase all-solid-state batteries are made of a single material which plays a role of the electrode and the electrolyte. Here, we demonstrate the properties for single-phase all-solid-state batteries we reported so far.*

Keywords: single-phase, all-solid-state battery, solid electrolyte, NASICON

1. INTRODUCTION

All-solid-state batteries have been recently expected for the next-generation energy storage devise since its solid electrolyte based on thio-LISICON family or glassy oxide material has demonstrated almost the same ionic conductivity (10^{-2} ~ 10^{-3} S cm^{-1}) to the liquid electrolyte. However, the interfacial resistance between electrode and electrolyte, which is almost one-order larger than the bulk resistance of solid electrolyte itself, is the biggest problem to commercialize the all-solid-state alkali-ion battery. The interfacial resistance is caused by the side reaction during the calcination, the space-charge layer, the mismatch of impedance and the insufficient contact between electrodes and electrolyte.

One of the essential solutions for eliminating the interfacial resistance is to use the same material for the solid electrolyte and electrodes. The concept of the battery consisting of a single-material, $Li_{10}GeP_2S_{12}$ (sulfide-based high ionic conductor), was first reported by Han et al [1], and it demonstrated significantly low interfacial resistance between electrode and electrolyte. However, sulfide is unfavorable for handling in the air because it reacts with water and generates H_2S gas which is indeed toxic. Therefore, we tried to convert the sulfide-based materials to the oxide-based materials. Among the oxide-based materials, NASICON (NA-ion Super Ionic CONductor)-type materials (Fig. 1) are known for their high ionic conductivity and large bottle-neck structure based on the corner-sharing framework. In addition, it is well known that NASICON is also suitable structure for intercalation host. Such advantages of NASICON-type materials realized the oxide-based single-phase all-solid-state batteries [2-5]. Table 1 shows the NASICON-type single-phase all-solid-state alkali-ion batteries reported by our group. Among them, we demonstrate the superior performances properties such as the high rate capability and the high operating voltage recently found in $Li_{1.5}Cr_{0.5}Ti_{0.5}(PO_4)_3$.

2. MATERIALS and METHODS

2.1 Materials selection

The materials must be satisfied 2 conditions; first is high ionic conductivity and second is to include transition metals. The materials of a single-phase all-solid-state battery have the role of the solid-electrolyte and electrodes. In order to realize rapid charge/discharge rate, the conductivity of the solid-electrolyte had better to be as large as possible. In this research, NASICON oxide materials are focused as the materials for the single-phase all-solid-state battery because they have high ionic conductivity due to its large bottle-neck structure based on the corner-sharing framework.

For the electrode function, NASICON materials are appropriate because they contain transition metals in the crystal structure. Moreover, the insertion/elimination reaction only occurs without any structure change in the charge/discharge process, so the cyclability can be expected. In addition, NASICON materials demonstrate the high redox potential due to an inductive effect caused by its poly-anionic structure.

For these reasons, we focused on NASICON materials as the main materials of the single-phase all-solid-state batteries.

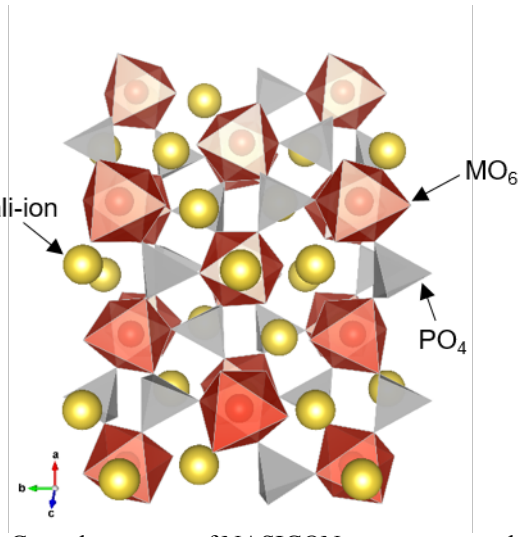

Fig. 1. Crystal structure of NASICON-type compounds.

2.2 Methods

The NASICON materials were synthesized by conventional solid phase methods. The materials containing vanadium were calcined under Ar + 5%H_2 in order to avoid the oxidation; and others were calcined under air. The samples were pelletized and annealed in

each appropriate temperature. For arranging as same thickness, the pellets were polished at 0.8 - 0.7 mm.
The X-ray diffraction (XRD) measurements (Cu Kα) were conducted using a Rigaku MiniFlex600 diffractometer. The scanning electron microscopy (SEM) analysis was performed using a JEOL JSM-6340F microscope. A thin platinum layer was sputtered on both sides of a sample pellet as a current collector. The cell was finally sealed into an HS cell (Hohsen Corp.) in an Ar-filled glove box.
The electrochemical charge/discharge measurements were performed using the galvanostatic method with a charge/discharge cycle instrument (BTS2400W, Nagano Electric Co.). The AC impedance measurements were executed under open-circuit conditions using an impedance analyzer over the frequency range from 1 MHz to 0.1 Hz.

3. RESULTS and DISCUSSION

Figure 2 shows the Arrhenius plots which is the temperature dependence of the electrical conductivity of alkali-ion NASICON-type materials. For these, $Li_{1.5}Cr_{0.5}Ti_{1.5}(PO_4)_3$ demonstrated the highest electric conductivity of 2×10^{-4} S cm^{-1} at 298 K. Furthermore, addition of Li_3BO_3 into $Li_{1.5}Cr_{0.5}Ti_{1.5}(PO_4)_3$ led enhancing the electric conductivity as shown in Fig. 2 because Li_3BO_3 worked as flux to fill the voids of $Li_{1.5}Cr_{0.5}Ti_{1.5}(PO_4)_3$ due to its lower melting point than those of NASICON materials [6]. SEM images in Fig. 3(a) and 3(b) visibly indicate that the Li_3BO_3 additive $Li_{1.5}Cr_{0.5}Ti_{1.5}(PO_4)_3$ pellet has higher density than the $Li_{1.5}Cr_{0.5}Ti_{1.5}(PO_4)_3$ pellet.

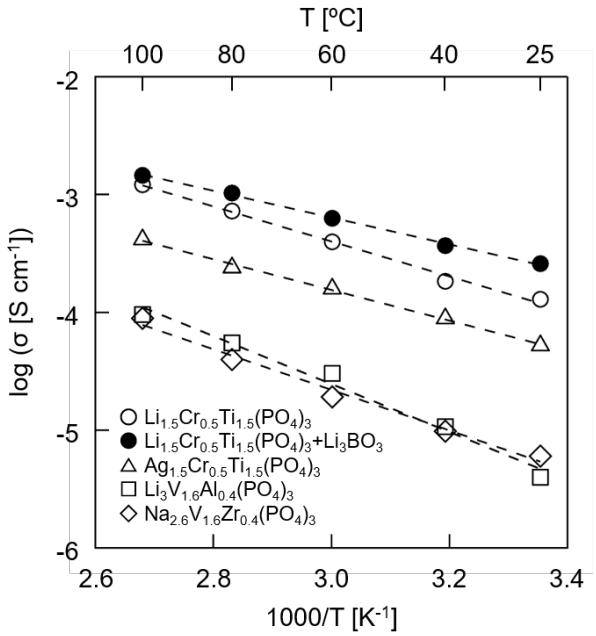

Fig. 2. Temperature dependence of the electrical conductivity of alkali-ion NASICON-type materials.

Table 1 shows the electric conductivity and the operating voltage with each current density for the NASICON-type all-solid-state alkali-ion battery cells. In the presentation, we will introduce the more detailed properties such as charge/discharge profiles and its electrode reaction.

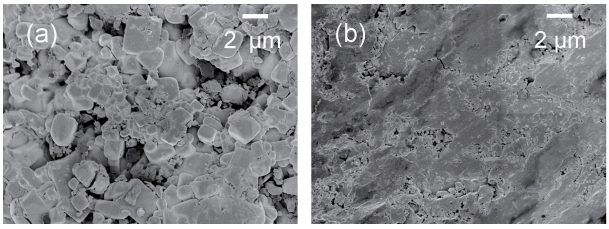

Fig. 3. SEM images of (a) $Li_{1.5}Cr_{0.5}Ti_{1.5}(PO_4)_3$ and (b)$Li_{1.5}Cr_{0.5}Ti_{1.5}(PO_4)_3$+$Li_3BO_3$ pellets.

Table 1. Typical NASICON-type all-solid-state alkali-ion batteries.

NASICON-type materials	Electrical conductivity (S cm^{-2})	Current density (mA cm^{-2})	Operating voltage
$Na_{2.6}V_{1.6}Zr_{0.4}(PO_4)_3$ [2]	5×10^{-6}	< 0.015	1.8 V
$Li_3V_{1.6}Al_{0.4}(PO_4)_3$ [3]	6×10^{-6}	< 0.015	1.7 V
$Li_{1.5}Cr_{0.5}Ti_{1.5}(PO_4)_3$ [4]	2×10^{-4}	0.1	2.2 V
$Ag_{1.5}Cr_{0.5}Ti_{1.5}(PO_4)_3$ [5]	5×10^{-5}	0.1	0.9 V

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