Effect of Li$_3$BO$_3$ addition to NASICON-type single-phase all-solid-state lithium battery based on Li$_{1.5}$Cr$_{0.5}$Ti$_{1.5}$(PO$_4$)$_3$

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All-solid-state Li-ion battery is expected as the post Li-ion battery because of its high reliability and safety. However, the biggest issue for the all-solid-state Li-ion battery is the interfacial resistance between electrode and electrolyte rather than the bulk ionic conductivity of the solid electrolyte. In order to reduce the interfacial resistance, we recently adopted a new concept, “single-phase all-solid-state battery”, which is made of a single material. In principle, single-phase all-solid-state battery has low interfacial resistance between the solid electrolyte and electrodes, because the solid electrolyte and electrodes are same material. Here, the electrochemical properties of single-phase all-solid-state battery based on Li$_{1.5}$Cr$_{0.5}$Ti$_{1.5}$(PO$_4$)$_3$ and the effect of Li$_3$BO$_3$ additive as flux to Li$_{1.5}$Cr$_{0.5}$Ti$_{1.5}$(PO$_4$)$_3$ are shown. The pellet of Li$_{1.5}$Cr$_{0.5}$Ti$_{1.5}$(PO$_4$)$_3$ with Li$_3$BO$_3$ additive showed higher density by filling the voids of Li$_{1.5}$Cr$_{0.5}$Ti$_{1.5}$(PO$_4$)$_3$. As the result of the low electronic conductivity of Li$_3$BO$_3$, the overpotential was increased. However, the electron leakage was suppressed. On the other hand, the operation voltage and the reversible capacity were improved due to the high lithium-ionic conductivity of Li$_3$BO$_3$. It was found that Li$_3$BO$_3$ additive is useful for the improvement of the single-phase battery.

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1. Introduction

Rechargeable all-solid-state lithium-ion batteries with inorganic solid electrolytes have been attracting special attention recently as next-generation secondary batteries due to their non-flammability and high volumetric energy density.\textsuperscript{1–4} Remarkably large ionic conductivity has been reported in sulfide-based solid electrolytes, which have lower Young’s moduli than oxide-based solid electrolytes.\textsuperscript{5–8} Dense sulfide-based electrolytes can thus be produced by cold pressing without a heating process to ensure sufficient contact between electrode and electrolyte materials. However, sulfide-based electrolytes potentially generate toxic H$_2$S due to reaction with water. In contrast, oxide-based solid electrolytes are rather stable in the atmosphere, although they have lower ionic conductivity and must be sintered at high temperature to achieve good contact between the electrode and electrolyte materials. Nevertheless, the reason why oxide-based all-solid-state batteries have not been put to practical use is that their interfacial resistance is much larger than their electrolyte resistance.\textsuperscript{9} One effective method to solve this problem is to construct a battery from a single material because we are released from the side reaction during preparation of the cell.\textsuperscript{10} In that case, a single material must play three roles as the cathode, anode and electrolyte. The advantage of such a battery is a dense interface between the electrode and electrolyte by high-temperature sintering without interdiffusion. We have recently reported some Na Super Ionic CONDuctor (NASICON)-type “single-phase” all-solid-state batteries that were fabricated from a single material.\textsuperscript{11–13} A single-phase all-solid-state battery using NASICON-type Li$_{1.5}$Cr$_{0.5}$Ti$_{1.5}$(PO$_4$)$_3$ (LCTP) exhibited higher lithium-ionic conductivity and operating voltage than the Li$_{1.5}$V$_{2-x}$Al$_x$(PO$_4$)$_3$-based single-phase all-solid-state battery we reported previously.\textsuperscript{13} As shown in Fig. 1, the LCTP single-phase all-solid-state battery exhibits charge–discharge reactions based on the redox reactions of the Cr$^{3+}$/Cr$^{4+}$ (cathode) and Ti$^{3+}$/Ti$^{4+}$ (anode), which results in an operating voltage of 2.2 V. However, LCTP has a low relative density, which results in low ionic conductivity.\textsuperscript{14} According to Aono et al., the addition of
Li$_3$BO$_3$ to LiTi$_2$(PO$_4$)$_3$ improves its density and ionic conductivity because Li$_3$BO$_3$ fills the voids in LiTi$_2$-(PO$_4$)$_3$. On the other hand, LCTP does exhibit slight electron leakage, which causes a low reversible capacity. It is expected that mixing of the Li$_3$BO$_3$ “pure ionic conductor” with LCTP would be effective to suppress this electron leakage, which would lead to a higher operating voltage and reversible capacity. In this paper, we report the effect of Li$_3$BO$_3$ addition to LCTP on the porosity, ionic conductivity and charge-discharge performance of the battery.

2. Experimental procedure

LCTP powder was stoichiometrically prepared using Li$_2$CO$_3$ (Wako Pure Chemical Industries, Ltd.), Cr$_2$O$_3$ (Wako Pure Chemical Industries, Ltd.), TiO$_2$ (Sigma Aldrich) and NH$_4$H$_2$PO$_4$ (Nacalai Tesque, Inc.) by the conventional solid-state reaction method. The mixture was sintered at 1273 K for 5 h in air. The product was then pelletized and annealed at 1373 K for 5 h in air. To prepare a LCTP–Li$_3$BO$_3$ composite pellet, LCTP powder and Li$_3$BO$_3$ powder (Toshima Manufacturing Co., Ltd.) were mixed in a molar ratio of 10:1, and annealed at 1273 K for 5 h in air. 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 (VersaSTAT3-400, AMETEC. Inc.) over the frequency range from 1 MHz to 0.1 Hz.

3. Results and discussion

Figure 2 shows XRD pattern of the formed pellets, which confirm the NASICON-type structure. The SEM images in Figs. 3(a) and 3(b) show that the LCTP–Li$_3$BO$_3$ pellet has higher density than the LCTP pellet. The relative densities of the LCTP and LCTP–Li$_3$BO$_3$ pellets were calculated based on the Archimedes’ method to be 80.1 and 91.9%, respectively. The relative density was increased due to Li$_3$BO$_3$ acting as binder and filling the pores. It is also noted that bulk density of the LCTP and LCTP–Li$_3$BO$_3$ pellets were 2.35 and 2.59 g/cm$^3$, respectively. Figure 3(c)
show the SEM-energy dispersive X-ray spectrometry (SEM-EDX) elemental mapping result of LCTP–Li3BO3 pellet. B elements are uniformly distributed. In some parts, B are distributed without P, indicating that formation of the bulky Li3BO3. For electrochemical measurements, the pellets were sputtered on both faces with Pt to function as a current collector.

Figures 4(a) and 4(b) show impedance plots for LCTP and LCTP–Li3BO3, respectively. The impedance spectra for both pellets had a semicircle and a spike in the low-frequency region. It should be noted that the measured conductivity includes not only ionic conductivity but also electronic conductivity because LCTP contains transition metals. Therefore, the measured conductivity is mixed conductivity. Figure 5 shows the temperature dependence of the electrical conductivity, from which LCTP–Li3BO3 pellet exhibited the highest electrical conductivity of $2.6 \times 10^{-4}$ S cm$^{-1}$ at 298 K, even though the electrical conductivity of LCTP was only $1.4 \times 10^{-4}$ S cm$^{-1}$. The observed electrical conductivity of LCTP–Li3BO3 pellet is still lower than the ionic conductivity of Li$_{1.5}$Cr$_{0.5}$Ti$_{1.5}$(PO$_4$)$_3$ (7 $\times$ 10$^{-4}$ S cm$^{-1}$). One of the important factors to increase conductivity is to increase the relative density. The relative density of the LCTP–Li3BO3 pellet was larger than that of LCTP pellet, which may indicate that the higher electrical conductivity of the Li$_{1.5}$Cr$_{0.5}$Ti$_{1.5}$(PO$_4$)$_3$–Li3BO3 pellet was due to its larger relative density. Figure 6 shows the first charge–discharge curves of the Pt/LCTP/Pt and Pt/LCTP–Li3BO3/Pt cells at room temperature. The Pt/LCTP–Li3BO3/Pt cell showed a larger overpotential than the Pt/LCTP/Pt cell. Some possible reasons for this are, first, increased electrode resistance due to the reaction of LCTP and Li3BO3. Second, the charge-transfer resistance is increased by the decrease in electronic conductivity by the addition of the pure lithium-ionic conductor, Li3BO3. On the other hand, the operating voltage of the Pt/LCTP–Li3BO3/Pt cell was higher than that of the Pt/LCTP/Pt cell. In addition, a larger reversible capacity was observed for the Pt/LCTP–Li3BO3/Pt cell. The cycling properties were also improved by the addition of Li3BO3 (Fig. 7). These results indicate that internal short circuiting is suppressed by the addition of Li3BO3. Generally, the lithium-ion transference number of the solid electrolyte is expressed according to the following equation:

$$E_R = t_i \times E_t$$  \hspace{1cm} (1)$$

where $E_R$ is the observed cell voltage, $t_i$ is the ionic transference number of the electrolyte, and $E_t$ is the theoretical cell voltage, respectively. Therefore, it is expected that ionic transport number of LCTP–Li3BO3 is larger than that of LCTP if the theoretical EMF is same. To compare the electronic conduction, the time-dependence of the open-circuit voltage (OCV) was measured after initial charging of 10 μAh at 0.1 mACm$^{-2}$ (Fig. 8). The decrease of the OCV is caused by self-discharge of the cell. Figure 8 shows that the Pt/LCTP–Li3BO3/Pt cell took a
longer time to completely short-circuit and decrease until 0 V than the Pt/LCTP/Pt cell. In other words, LCTP–Li$_3$BO$_3$ has less electronic conductivity than LCTP. Considering both the results of the electrical conductivity measurements and the self-discharge profiles, it is obvious that the lithium-ionic conductivity was increased and the electronic conductivity decreased by the addition of Li$_3$BO$_3$ to LCTP. We consider that Li$_3$BO$_3$ suppressed the electronic conducting paths and increased the ionic conducting paths because Li$_3$BO$_3$ has a low melting point and does not exhibit electron conductivity.

4. Conclusion

In conclusion, single-phase all-solid-state lithium-ion batteries were prepared using LCTP, and the effect of Li$_3$BO$_3$ addition to LCTP was investigated. The density and the lithium-ion transference number of LCTP was successfully improved by Li$_3$BO$_3$, although the overpotential of the battery cells increased. It was also confirmed that the operation voltage and the reversible capacity increased due to the increase of the lithium-ion transference number. Suppression of the electron leakage was observed by the addition of Li$_3$BO$_3$ to LCTP. Therefore, it is expected that Li$_3$BO$_3$ addition will be an effective approach to improve the properties of single-phase all-solid-state lithium-ion batteries with mixed conducting materials. In future research, we will elucidate the mechanism for the increased lithium-ionic conductivity by Li$_3$BO$_3$ addition and the effect of compositing lithium salt into battery materials.

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