Effect of Na_3BO_3 Addition into $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ Single-Phase All-Solid-State Batteries

Akira NISHIO,^{a,§} Nobuaki SHIRAI,^a Hironari MINAMI,^b Hiroaki IZUMI,^b
Atsushi INOISHI,^{c,*§§} and Shigeto OKADA^{c,§§}

^a Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasuga-koen, Kasuga, Fukuoka 816-8580, Japan

^b Suzuki Motor Corporation, Automobile Electrical Design Department, Hamamatsu, Shizuoka 432-8611, Japan

^c Institute for Materials Chemistry and Engineering, Kyushu University, 6-1 Kasuga-koen, Kasuga 816-8580, Japan

* Corresponding author: inoishi@cm.kyushu-u.ac.jp (A. I.)

ABSTRACT

To reduce the interfacial resistance between the electrodes and electrolyte in all solid-state battery, we have recently suggested the idea of a single-phase all-solid-state battery that is made from a single material with the three roles of electrolyte, positive electrode and negative electrode. In this research, the effects of Na_3BO_3 addition into $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ were investigated with respect to the electrochemical properties. Na_3BO_3 addition improved the relative density of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ by acting as a flux to fill the voids of the sintered body, as confirmed by scanning electron microscopy (SEM) observations. The electrical conductivity is increased by the addition of Na_3BO_3 , although the activation energy is also increased. Charge/discharge measurement revealed that $\text{Na}_3\text{V}_2(\text{PO}_4)_3+\text{Na}_3\text{BO}_3$ pellets exhibit improved cyclability and optical observation indicated a different mechanism for the in-situ formation of the electrode from a $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ pellet.

© The Author(s) 2021. Published by ECSJ. This is an open access article distributed under the terms of the Creative Commons Attribution Non-Commercial Share Alike 4.0 License (CC BY-NC-SA, <http://creativecommons.org/licenses/by-nc-sa/4.0/>), which permits non-commercial reuse, distribution, and reproduction in any medium by share-alike, provided the original work is properly cited. For permission for commercial reuse, please email to the corresponding author. [DOI: 10.5796/electrochemistry.21-00023].

Keywords : Single-phase, All-solid-state Batteries, Na-ion Batteries, NASICON

1. Introduction

Due to the demand for large-scale grid storage applications, sodium ion batteries have attracted attention as one of the candidates for post Li-ion batteries due to their inexpensiveness and the abundance of resources on the Earth.^{1–3} The demand for safe batteries has also increased and all-solid-state batteries have been considered as one of the safest battery types due to the use of inorganic solid electrolytes, which are nonflammable materials, in contrast to conventional batteries that employ flammable organic electrolytes.^{4–6} Furthermore, sulfide materials in sulfide based batteries can react with oxygen and moisture in the air and emit harmful SO_x and H_2S . Therefore, oxide-based all-solid-state batteries promise to be the safest batteries due to their non-flammability and atmospheric stability. Many types of oxide-based solid electrolytes have been studied for application to Li-ion batteries. On the other hand, there have been few studies on novel oxide-based Na-ion conductors, such as $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ (NZSP), which is a Na-ion Super Ionic CONductor (NASICON)-type compound, and $\beta\text{-Al}_2\text{O}_3$.^{7–9} The main problem with the oxide-based all-solid-state batteries is the interfacial resistance between the solid electrodes and solid electrolyte. The interfacial resistance is caused by the impedance mismatch, space charge layer and impurity formation due to side reactions between the electrodes and solid electrolyte materials during high-temperature firing.^{5,10} To overcome such difficulties, we have focused on a new battery system termed a single-phase all-solid-state battery, which is constructed from a single material that has all the functions of the positive electrode, negative electrode and electrolyte.^{11–15} For single-phase all-solid-

state batteries, the electrodes must be formed in-situ from the solid electrolyte by current flow. Some in-situ formed electrodes have been investigated, and the $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{TiO}_2-\text{P}_2\text{O}_5$ glass ceramics sheet, which has a similar composition to the $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ti}_{1.5}(\text{PO}_4)_3$ NASICON-type Li-ion conductor, has been investigated the most.^{16–18} NASICON-type materials have an ideal crystal structure for single-phase all-solid-state batteries due to their wide bottle neck and facile substitution by elements such as alkali metals and transition metals.⁸ One of the NASICON-type materials, $\text{Na}_{3-x}\text{V}_{2-x}\text{Zr}_x(\text{PO}_4)_3$, has been reported to possess the properties of Na-ion migration for single-phase all-solid-state batteries, and has exhibited reasonable characteristics for solid electrolyte and electrodes.¹² To further improve the properties, we have also reported the addition of a lithium salt, Li_3BO_3 , which has a low melting point, to a single-phase all-solid-state Li-ion battery that uses $\text{Li}_{1.5}\text{Cr}_{0.5}\text{Ti}_{1.5}(\text{PO}_4)_3$. The ionic conductivity and the charge/discharge properties were successfully increased by filling the voids of the high porosity $\text{Li}_{1.5}\text{Cr}_{0.5}\text{Ti}_{1.5}(\text{PO}_4)_3$ sintered body with Li_3BO_3 which is a Li-ionic conductor.¹⁹

In this work, we investigated the effect of Na_3BO_3 (NBO) addition into $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (NVP) to improve the properties of NVP for application as a single-phase all-solid-state battery. NVP has previously been reported to exhibit battery properties with the mechanism shown in Fig. 1.¹² NVP and NBO were synthesized and characterized as the precursor for a sintered body. The precursors were mixed in certain ratios, and the addition of NBO was evaluated with respect to the resultant electrochemical properties of NVP. Optical observation was employed at the end of this research to confirm if the NBO additive and the porosity of the pellets had an effect on the in-situ formation of the electrodes.

2. Experimental

2.1 Materials synthesis

NVP powder and NBO powder were synthesized by the

[§]ECSJ Student Member

^{§§}ECSJ Active Member

A. Nishio orcid.org/0000-0003-2348-4098

A. Inoishi orcid.org/0000-0001-7774-2502

S. Okada orcid.org/0000-0002-8944-1990

Figure 1. Schematic model of an NVP-based single-phase all-solid-state battery cell.

conventional solid-state reaction method. NaH_2PO_4 (Fujifilm Wako; min 99.0 %) and V_2O_5 (Fujifilm Wako; min 99.0 %) were mixed in a stoichiometric ratio by hand milling in an agate mortar as the raw materials for NVP. The mixture was then sintered at 900 °C for 20 h under $\text{Ar}+5\% \text{H}_2$ gas flow for reduction of the valence of vanadium from pentavalent to trivalent. The fired mixture was crushed and sintered again under the same conditions to obtain single-phase NVP. NBO was synthesized in an Ar-filled glove box using NaOH (Fujifilm Wako; 97.0 %) and H_3BO_3 (Fujifilm Wako, min; 99.5 %) which were dried under vacuum at 350 °C before being placed in the glove box. The primary materials were mixed and calcined at 400 °C for 4 h. The precursor was then crushed and sintered at 450 °C for 2 h.

2.2 Pelletization

NVP powder and NBO powder were mixed in molar ratios of 95 : 5, 90 : 10 and 85 : 15 by hand-milling with an agate mortar in an Ar-filled glove box. The precursor powder was uniaxially pressed at 255 MPa and then isostatically pressed at 300 MPa after packing the pellets in a plastic cover under vacuum. The pellets were annealed at 900 °C or 800 °C for 5 h in an $\text{Ar}+5\% \text{H}_2$ atmosphere on a precursor powder bed on an alumina plate. The pellets obtained were polished with sandpaper to adjust the thickness to between 0.7 and 0.8 mm. The ball-milled precursor powder was also supplementary employed to improve the electrical conductivity of the pellets. The precursor was ball-milled at 150 rpm for 3 h using a planetary mill (Pulverisette 7, Fritsch).

2.3 Materials characterization

X-ray diffraction (XRD) data for NVP, NBO and the pellets were collected to identify the crystal structure at room temperature using an X-ray diffractometer (Miniflex 600, Rigaku) with $\text{CuK}\alpha$ radiation. The samples were measured in steps of 0.01° in the 2θ angular range of 10–80° at a scan rate of 10° min^{−1}. The morphology and composition of the NVP, NBO and pellet samples were obtained using scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS; NeoScope JCM-7000, JEOL) analysis.

2.4 Electrochemical characterization

Thin platinum layers were sputtered on both sides of a sample pellet as current collectors. The pellets were then evacuated at 150 °C to remove any moisture and oxygen. An HS cell (Hohsen Corp.) was employed for all electrochemical measurements. All the cells were assembled in an Ar-filled glove box (dew point < −80 °C). Impedance measurements were performed using an impedance analyzer (SP-300; Biologic) in the frequency range of 0.1 Hz to 7 MHz at temperatures from 25 °C to 120 °C. Impedance fitting was conducted using equivalent circuit modeling software (ZView, Scribner Associates, Inc.). Charge and discharge measurements were performed using a galvanostatic instrument (HJ1020mSD8, Hokuto Denko) at 100 °C. The current density was 15 μA cm^{−2} and the capacity was regulated to 30 μAh to

maintain a constant state of charge each time because the single-phase all-solid-state battery did not have a clear electrode area.

2.5 Investigation of the in-situ formed electrode

The in-situ formed electrode was investigated by observation of the surface on the negative electrode side of a charged pellet because compared to the initial color of the pellet, the color of the negative electrode side changed much more than that of the positive electrode side. The NVP and NVP+NBO pellets were charged to 3.0 V at 0.015 mA cm^{−2} and then removed from the HS cell in air. The pellets were immediately observed and optical micrographs were obtained, and SEM and an EDS mapping system were employed. The surface of the pellets was observed at an arbitrary thickness using sandpaper to slightly polish the surface of the pellets until there were no color-changed areas which was the maximum area that the in-situ electrode formed.

3. Result and Discussion

NVP and NBO powders were synthesized by the conventional solid-state reaction method following the procedures given in the experimental section. The XRD profiles for NVP and NBO powder are presented with the ICSD for $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (No. 248140; $R3c$) and Na_3BO_3 (No. 1351; $P12_1/c1$) in Fig. S1 of the Supporting Information (SI). The XRD pattern for as-synthesized NVP was consistent with the ICSD for $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ with a secondary phase of V_2O_5 . The as-synthesized NBO was confirmed to be single phase. The NVP+NBO (85 : 15) pellet was annealed at 800 °C because the pellet sintered at 900 °C adhered to the alumina plate and was difficult to remove. Figure 2 shows XRD patterns for the NVP and the NVP+NBO pellets with NVP : NBO mixing ratios of 95 : 5, 90 : 10 and 85 : 15. The NVP phase was observed in the XRD profiles for all of the NVP+NBO pellets, and trace amounts of an unknown impurity were confirmed, the peak intensity of which increased with the amount of added NBO. In addition, it is assumed that no NBO phase was observed due to its amorphization by high-temperature annealing.

The relative densities of the NVP and NVP+NBO pellets were calculated based on the Archimedes method and the results are shown in Fig. 3(a). The addition of NBO to NVP increased the relative density of the sintered pellets; however, excess addition such as > 15 % NBO was not as effective as the addition of 5 % and 10 % NBO. The relative densities of the NVP and NVP+NBO (95 : 5, 90 : 10 and 85 : 15) pellets were 77.3, 81.7, 86.7 and 81.1 %, respectively. Figures 3(b) and 3(c) show SEM images of the NVP and NVP+NBO (95 : 5) pellets. The voids in the NVP+NBO pellet were more filled than those in the NVP pellet. The reduction of voids by the addition of NBO to NVP as shown in the SEM images is consistent with the increase in the relative densities of the NVP+NBO pellets.

Figures 4(a) and 4(b) show Nyquist plots and Arrhenius plots of the total electrical conductivity (σ_{total}) for the Pt/NVP/Pt and Pt/NVP+NBO(95 : 5)/Pt cells. The mixing ratio of NVP : NBO =

Figure 2. XRD profiles for the as-synthesized NVP powder and NVP+NBO pellets for each mixing ratio (NVP : NBO = 100 : 0, 95 : 5, 90 : 10, 85 : 15).

Figure 3. (a) Relative densities of the NVP and the NVP+NBO pellets (95 : 5, 90 : 10 and 85 : 15). Cross-sectional SEM micrographs of the (b) NVP and (c) NVP+NBO pellets.

Figure 4. (a) Nyquist plots measured at 25 °C, (b) Arrhenius plots of the total electrical conductivity (σ_{total}), and (c) Arrhenius plots of the bulk (σ_{bulk}) and grain boundary (σ_{gb}) electrical conductivity for the Pt/NVP/Pt and Pt/NVP+NBO/Pt cells.

95 : 5 was the optimum ratio and this pellet showed the highest conductivity among the NVP+NBO pellets, as shown in Table S1 of the SI. Note that the conductivity of the NVP pellet is not indicated as ionic conductivity but as electrical conductivity, which is the sum of the ionic conductivity and electronic conductivity, because NVP is not only an ionic conductor but also an electrical conductor because the 3d transition metal vanadium is included. From this point on, all measurements were performed using

NVP+NBO pellets with a mixing ratio of 95 : 5. In Fig. 4(a), the total resistance was calculated as the value of the sum for the bulk resistance and the grain boundary resistance. Two capacitive semicircles were apparent for the Pt/NVP/Pt and the Pt/NVP+NBO/Pt cells, while three capacitive semicircles were most suitable for fitting the impedance as a result of the bulk resistance, the grain boundary resistance and the contact resistance between the pellet and Pt film current collectors, as shown in Fig. S2 of the SI.

Table 1. Bulk, grain boundary and total electrical conductivity of the NVP and NVP+NBO (95 : 5) pellets (σ = electrical conductivity, gb = grain boundary).

	NVP@25 °C (S cm ⁻¹)	NVP+NBO@25 °C (S cm ⁻¹)	NVP@100 °C (S cm ⁻¹)	NVP+NBO@100 °C (S cm ⁻¹)	E_a (NVP) (eV)	E_a (NVP+NBO) (eV)
σ_{bulk}	5.6×10^{-7}	6.0×10^{-6}	7.9×10^{-6}	9.4×10^{-5}	0.37	0.37
σ_{gb}	9.6×10^{-7}	2.3×10^{-6}	1.6×10^{-5}	2.0×10^{-4}	0.34	0.60
σ_{total}	3.5×10^{-7}	1.7×10^{-6}	5.3×10^{-6}	6.5×10^{-5}	0.35	0.49

Figure 5. (a) Charge-discharge profiles and (b) cycling properties measured at 100 °C for the Pt/NVP/Pt and Pt/NVP+NBO/Pt cells as single-phase all-solid-state batteries.

Figure 4(b) compares Arrhenius plots of the total electrical conductivity (σ_{total}) for the NVP and NVP+NBO pellets; the slope for the NVP+NBO pellet was steeper than that for the NVP pellet, suggesting that the activation energy was increased by the addition of NBO to NVP. For more detailed analysis, impedance fitting was conducted for each temperature, and the electrical conductivities and activation energies were calculated based on the bulk resistance and grain boundary resistance. The bulk, grain boundary and total electrical conductivities (σ_{bulk} , σ_{gb} , σ_{total} , respectively) and the activation energy (E_a) for the NVP and NVP+NBO pellets are given in Table 1. The Arrhenius plots of σ_{bulk} and σ_{gb} for the NVP and NVP+NBO pellets are shown in Fig. 4(c). σ_{total} was improved from 4.9×10^{-6} S cm⁻¹ to 8.5×10^{-5} S cm⁻¹ at 100 °C, and σ_{bulk} and σ_{gb} were also increased at each temperature by the addition of NBO to NVP. On the other hand, $E_{a \text{ total}}$ for the NVP+NBO pellet was larger than that for the NVP pellet, although $E_{a \text{ bulk}}$ was the same for both the NVP and NVP+NBO pellets. The increase in $E_{a \text{ total}}$ was most likely due to the doubling of $E_{a \text{ gb}}$. These results could be due to the addition of NBO with a lower melting point, which filled the voids between NVP particles, but also increased the transfer barrier for Na ions as the ions pass through the NVP particles to the NBO particles with lower ionic conductivity. In addition, as shown in Table S1 of the SI, the electrical conductivity was successfully improved by the ball-milling process before pelletization due to the decrease in the grain size of the precursor powder.

Figures 5(a) and 5(b) shows charge/discharge curves and the cycling properties for the Pt/NVP/Pt and Pt/NVP+NBO/Pt cells as single-phase all-solid-state batteries. The charge capacity was regulated to 30 μAh to maintain a constant state of charge each time because the single-phase all-solid-state battery did not have a clear electrode area, and the progressing area of the in-situ formed electrode was varied in each experiment in the measurement by potential regulation. The average charge/discharge voltage at ca. 1.7 V was almost comparable to the NVP half-cell data, where the V³⁺/V⁴⁺ and V²⁺/V³⁺ redox reactions had plateaus at 3.4 and 1.7 V vs. Na/Na⁺, respectively.²⁰ In addition, the overpotential was suppressed by the addition of NBO, which corresponds to the results

of the impedance measurements, where the total resistance decreased and the potential loss due to the IR drop was reduced by the addition of NBO. The effect of NBO addition was also evident in the improvement of the charge-discharge cycle properties. The discharge capacity of the Pt/NVP/Pt cell rapidly decreased after the third cycle, while that of the Pt/NVP+NBO/Pt cell increased after each cycle. The increase in the discharge capacity of the Pt/NVP+NBO/Pt cell peaked around 23 μAh during charge/discharge cycling, which could be due to hysteresis of the charge/discharge process in the NVP material. The cause of the increase in the reversible capacity of the Pt/NVP+NBO/Pt cell by cycling should be clarified in future research.

Figure 6(a) shows charge profiles of the Pt/NVP/Pt and Pt/NVP+NBO/Pt cells under a terminal charge voltage of 3 V. The Pt/NVP+NBO/Pt cell showed a larger charge capacity of 168 μAh than the Pt/NVP/Pt cell at 144 μAh. SEM images and EDS mapping images for the negative electrode side of a charged Pt/NVP/Pt pellet are shown in Figs. 6(b)–6(d), and those for the surface of the initial pellet and the positive electrode side after charging are shown in Figs. S3(a)–S3(f). Compared with the EDS maps, the dark areas in the SEM image of the negative electrode side indicate the presence of excess Na and little V, which suggests that Na⁺ ions had migrated to a specific place on the negative electrode side. On the other hand, no color change was observed on the positive electrode side, although a decrease in the amount of Na was observed in the central part of the positive electrode side. Therefore, we focused on the color change of the negative electrode side to compare the in-situ formed electrode between NVP and NVP+NBO.

Figures 6(e)–6(f) show optical micrographs of the surface of the negative electrode side of the Pt/NVP/Pt and Pt/NVP+NBO/Pt pellets after charging under a terminal charge voltage of 3 V. For the initial Pt/NVP/Pt pellet, the surface was a bright green color, as shown in Fig. S4, while the area appeared black after the charging process. Moreover, the Pt/NVP+NBO/Pt pellet showed larger and more dense black areas. The black areas in the optical microscopy images corresponded with the dark areas in the SEM image, which

Figure 6. (a) Charge profiles for the Pt/NVP/Pt and Pt/NVP+NBO/Pt cells under a terminal charge voltage of 3 V at 100 °C. (b) SEM micrograph and EDS maps for (c) Na and (d) V on the Pt/NVP/Pt pellet. Optical micrographs of the surface on the negative electrode side of the (e) Pt/NVP/Pt and (f) Pt/NVP+NBO/Pt pellets after the charge process at a terminal voltage of 3 V at arbitrary thicknesses by polishing with sandpaper until the surface of the pellets showed no color-change areas.

indicated that these were regions with large distributions of Na. The results were different after polishing away the surface of the negative electrode side for the Pt/NVP/Pt and Pt/NVP+NBO/Pt cells. For the Pt/NVP/Pt cell, a 112 μm thick layer was removed until the dark color area disappeared. On the other hand, for the Pt/NVP+NBO/Pt cell, only a 20 μm thick layer was removed until the dark colored area disappeared. Therefore, the Pt/NVP/Pt cell formed a deep in-situ electrode over a small area, while the Pt/NVP+NBO/Pt cell formed a homogeneous shallow thickness in-situ electrode over a wide area. This phenomenon may be due to the many voids in the NVP pellet, so that the current passes through only a limited area, which results in the formation of a narrow and deep electrode, and a low charge capacity, whereas the NVP+NBO pellet has a high degree of densification and the current is applied evenly over a wider area. This resulted in the higher charge capacity of the Pt/NVP+NBO/Pt cell than that of the Pt/NVP/Pt cell.

4. Conclusion

The addition of NBO to NVP was effective for improving the battery properties of a single-phase all-solid-state Na-ion battery. NVP and NBO powder were successfully synthesized and the optimal amount of NBO addition to NVP was determined to be 5 %. The voids in the NVP sintered body were filled by NBO powder according to SEM observations, which increased the relative density of NVP+NBO pellets compared to the NVP pellets. The NVP+NBO (90 : 10) pellets had the highest relative density; however, the NVP+NBO (95 : 5) pellets exhibited the highest electrical conductivity of $8.5 \times 10^{-5} \text{ S cm}^{-1}$. On the other hand, the

activation energy for the total and grain boundary was increased due to the low ionic conductivity of NBO and the generation of the grain boundaries between NVP and NBO. The Pt/NVP+NBO/Pt cell exhibited excellent cyclability compared to the Pt/NVP/Pt cell, although the charge/discharge profiles showed a lower reversible capacity at the first cycle for NVP+NBO. The 3 V terminal charge voltage measurements revealed that the Pt/NVP+NBO/Pt cell showed larger capacity than the Pt/NVP/Pt cell, and excess Na^+ was observed at the surface of the negative electrode side of the cells after 3 V charging. The in-situ formation of the electrodes differed depending on the porosity of the pellets; it suggested that electrochemical reactions occur in more narrow and deep regions when the porosity is high, and in more wide and shallow thickness regions when the porosity is low and the pellets are dense. While NBO may be a potential barrier to electron conduction, the density is much more important for both the cyclability and reversible capacity of the in-situ formed electrode.

Supporting Information

The Supporting Information is available on the website at DOI: <https://doi.org/10.5796/electrochemistry.21-00023>.

Acknowledgments

This work was financially supported by MEXT, Japan (Grant-in-Aid for Scientific Research on Innovative Areas (JP20H05297), ESICB program (JPMXP0112101003) and “Five-star Alliance”).

References

1. J.-M. Tarascon, *Nat. Chem.*, **2**, 510 (2010).
2. B. Dunn, H. Kamath, and J.-M. Tarascon, *Science*, **334**, 928 (2011).
3. K. Kubota and S. Komaba, *J. Electrochem. Soc.*, **162**, A2538 (2015).
4. M. Tatsumisago, M. Nagao, and A. Hayashi, *J. Asian Ceram. Soc.*, **1**, 17 (2013).
5. K. Takada, *J. Power Sources*, **394**, 74 (2018).
6. M. Shoji, E. J. Cheng, T. Kimura, and K. Kanamura, *J. Phys. Appl. Phys.*, **52**, 103001 (2019).
7. J. B. Goodenough, H. Y.-P. Hong, and J. A. Kafalas, *Mater. Res. Bull.*, **11**, 203 (1976).
8. C. Masquelier and L. Croguennec, *Chem. Rev.*, **113**, 6552 (2013).
9. X. Lu, G. Xia, J. P. Lemmon, and Z. Yang, *J. Power Sources*, **195**, 2431 (2010).
10. K. Takada, *Langmuir*, **29**, 7538 (2013).
11. F. Han, T. Gao, Y. Zhu, K. J. Gaskell, and C. Wang, *Adv. Mater.*, **27**, 3473 (2015).
12. A. Inoishi, T. Omuta, E. Kobayashi, A. Kitajou, and S. Okada, *Adv. Mater. Interfaces*, **4**, 1600942 (2017).
13. A. Inoishi, T. Omuta, Y. Yoshioka, E. Kobayashi, A. Kitajou, and S. Okada, *ChemistrySelect*, **2**, 7925 (2017).
14. A. Inoishi, A. Nishio, Y. Yoshioka, A. Kitajou, and S. Okada, *Chem. Commun.*, **54**, 3178 (2018).
15. A. Inoishi, A. Nishio, A. Kitajou, and S. Okada, *ChemistrySelect*, **3**, 9965 (2018).
16. C. Yada, Y. Iriyama, T. Abe, K. Kikuchi, and Z. Ogumi, *J. Electrochem. Soc.*, **153**, A1148 (2006).
17. Y. Iriyama, C. Yada, T. Abe, Z. Ogumi, and K. Kikuchi, *Electrochem. Commun.*, **8**, 1287 (2006).
18. T. Yamamoto, Y. Sugiura, H. Iwasaki, M. Motoyama, and Y. Iriyama, *Solid State Ionics*, **337**, 19 (2019).
19. A. Nishio, A. Inoishi, A. Kitajou, and S. Okada, *J. Ceram. Soc. Jpn.*, **127**, 18 (2019).
20. Y. Uebou, T. Kiyabu, S. Okada, and J. Yamaki, *The Reports of Institute of Advanced Material Study Kyushu University*, **16**, 1 (2002).