Reuse of the surrounding powder used as a Na-source in the fabrication of sodium-beta–alumina solid electrolyte by vapor-phase conversion method

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Highlights

- Na/NiCl$_2$ secondary batteries are not widely commercialized due to their high prices.

- Flat-structured cells are proposed as an approach that could lower the price of Na/NiCl$_2$ batteries by enabling production automation.

- Thin disk-shaped Na$^+–\beta/\beta'–$Al$_2$O$_3$ solid electrolyte, which is used as a core material in planar Na/NiCl$_2$ batteries, is manufactured by a vapor phase conversion process.

- During the vapor phase conversion process, large amounts of surrounding powder are used as a sodium source, which are usually used once and then discarded.

- This study shows that once-used surrounding powder can be reused several more times.
Abstract

While Na/NiCl$_2$ secondary batteries offer high safety and excellent performance, their high price inhibits their commercialization. Two approaches are proposed to solve this problem: (1) automatic production by making cells of a flat plate structure, and (2) lowering the price of sodium-beta-alumina solid electrolyte (BASE), a key component. In general, a thin and wide disk-type BASE for a planar Na/NiCl$_2$ battery is prepared from zirconia-toughened alumina (ZTA) by a vapor-phase conversion (VPC) process. In the process, Na–β"–Al$_2$O$_3$ powder, which is usually used as surrounding powder to supply sodium, is used once, then discarded. In this study, two methods were attempted to reduce the BASE cost fabricated by the VPC process. The first is the reuse of the surrounding powder in the VPC. The number of reuses has been up to three times. The second is that the surrounding powder is used as-is by mixing raw material powders, that is α–Al$_2$O$_3$, Na$_2$CO$_3$, and Li$_2$CO$_3$, instead of Na–β"–Al$_2$O$_3$ powder. This allows omission of the calcination process required for Na–β"–Al$_2$O$_3$ synthesis. Furthermore, the properties of the BASE prepared by VPC with the reused surrounding powder were analyzed, and their changes were investigated.

KEY WORDS: Sodium-beta–alumina, Na/NiCl$_2$ battery, ZEBRA battery, Vapor phase conversion, Beta–alumina solid electrolyte
Introduction

The NaNiCl$_2$ secondary battery with high energy density and charge/discharge efficiency is used for the large capacity energy storage system (ESS). The Na/NiCl$_2$ battery is therefore an ideal choice for the next-generation battery, as it offers an effective solution to the safety problem of the lithium ion battery (LIB). The Na/NiCl$_2$ battery consists of nickel and sodium chloride as cathode electrode, sodium metal as anode electrode, and a ceramic solid electrolyte made from sodium–ion-conducting Na$^{+}$β/β”–Al$_2$O$_3$ (BASE). This means that there is no risk of fire from side reactions during cell operation, since the resulting product is NaCl. Moreover, the cost of the active materials is low, due to their abundant reserves [1,2]. While the Na/NiCl$_2$ battery has several benefits, their manufacturing costs are more expensive than the LIB. Since ceramic solid electrolyte is used, the operating temperature is high, at above 300 °C or so. Therefore, the price of the battery parts is very high, because parts of the cell need to be heat-resistant [3,4].

To reduce the operating temperature, the thickness of the BASE needs to be reduced to achieve high sodium ion conductivity, even at low temperatures. However, in the conventional design of the Na/NiCl$_2$ battery, specifically the tubular type, it was necessary to reduce the thickness of BASE through costly post-processing steps after sintering. To address these issues, research is underway to modify the battery design to a planar type (Fig. 1), and manufacture the BASE in the form of a thin disk, aiming to overcome the challenges associated with the high post-processing costs in the tubular design. [5-7]

To manufacture a thin BASE, it is necessary to produce a precursor material, zirconia-toughened alumina (ZTA), in a thin form, and subsequently fabricate it using a method termed vapor phase conversion (VPC), supplying sodium ions at temperatures below 1,450 °C [8-13].
Fig. 1. The 5 Wh class planar Na/NiCl2 battery cell (left), and its major components (right) [14].

The BASE is a sodium ion conductor that has high ionic conductivity. It consists of two distinctive phases: $\beta$–Al$_2$O$_3$ (NaAl$_{11}$O$_{17}$) and $\beta''$–Al$_2$O$_3$ (NaAl$_5$O$_8$); Fig. 2 shows that because of the different structures and sodium contents, the ionic conductivity of the $\beta''$–Al$_2$O$_3$ is $(3–10)$ times higher than that of the $\beta$–Al$_2$O$_3$ [14–19]. The BASE is synthesized through various process, such as the solid state reaction, sol–gel process, and VPC.

Fig. 2. Crystal structure of the Na$^+$–$\beta/\beta''$–Al$_2$O$_3$: (a) Na$^+$–$\beta$–Al$_2$O$_3$, (b) Na$^+$–$\beta''$–Al$_2$O$_3$ [20].

The solid state reaction is widely used commercially because of its suitability for mass production. However, due to the high sintering temperature of $1,600 \, ^\circ C$ or higher, the vapor pressure of Na$_2$O is relatively high, and significant loss of Na$_2$O can occur through the vapor phase.

In addition, it is vulnerable to atmospheric moisture and CO$_2$ due to the formation of NaAlO$_2$ secondary phase. The reaction between the interfacial NaAlO$_2$ and moisture involves dissolution, while the reaction with CO$_2$ involves the formation of Na$_2$CO$_3$. In both cases, cracking and delamination occur along the grain boundaries.

The sol–gel process has limitations for industrialization, due to the decreased mechanical strength and high cost associated with raw materials and synthesis [21].

The vapor phase conversion reacts solid $\alpha$–Al$_2$O$_3$ with Na$_2$O in the vapor phase to form Na$^+$–$\beta/\beta''$–Al$_2$O$_3$. The Na$^+$–$\beta/\beta''$–Al$_2$O$_3$ that forms on the surface of $\alpha$–Al$_2$O$_3$ acts as a good Na$^+$ ion conductor. Although Na$^+$ ions can quickly diffuse through the Na$^+$–$\beta/\beta''$–Al$_2$O$_3$, O$^2-$ ions diffuse
very slowly through $\text{Na}^+–\beta/\beta''–\text{Al}_2\text{O}_3$. Therefore, pure $\alpha$-$\text{Al}_2\text{O}_3$ is not used as a precursor for VPC when preparing $\text{Na}^+–\beta/\beta''–\text{Al}_2\text{O}_3$. As known, yttria-stabilized zirconia (YSZ) provides a fast route for $\text{O}^2−$ ion transport. When using the $\alpha$-$\text{Al}_2\text{O}_3$/YSZ sintered composite (i.e. ZTA), it allows coupled diffusion of $\text{Na}^+$ through the $\text{Na}^+–\beta/\beta''–\text{Al}_2\text{O}_3$, and $\text{O}^2−$ through YSZ, thus facilitating phase conversion to $\text{Na}^+–\beta/\beta''–\text{Al}_2\text{O}_3$ [22]. Fig. 3 shows the VPC process. The VPC process can improve the disadvantages of the two methods described above, and can be manufactured in the form of a thin film, making it suitable as a solid electrolyte for medium-to low-temperature planar cells below 200 °C.

**Fig. 3.** (a) Schematic illustration and (b) SEM imagery of the cross sectional surface morphology of the conversion process from $\alpha$-alumina/YSZ composite to $\text{Na}^+–\beta/\beta''$-alumina/YSZ composite electrolyte by VPC [22,23].

When manufacturing BASE by the VPC method, sodium must be supplied to the ZTA precursor in gaseous form. $\text{Na}^+–\beta''–\text{Al}_2\text{O}_3$ powder is used as a sodium source known so far, and the VPC process is performed by surrounding ZTA with a sufficient amount of $\text{Na}^+–\beta''–\text{Al}_2\text{O}_3$ powder [8-13]. In this study, a mixture of $\alpha$–$\text{Al}_2\text{O}_3$, $\text{Na}_2\text{CO}_3$, and $\text{Li}_2\text{CO}_3$, which are the raw material powders for this surrounding powder, was used directly without synthesis process. When $\text{Na}_2\text{CO}_3$ is used as a surrounding powder, molten $\text{Na}_2\text{CO}_3$ sticks to the BASE surface due to its low melting point (850 °C). In this study as well, the same problem occurred as shown in Fig. 4. However, this problem could be solved by manufacturing and using the surrounding powder as green pellet, which is a disc-shaped surrounding powder made by pressing a mixture of the raw material powders $\alpha$–$\text{Al}_2\text{O}_3$, $\text{Na}_2\text{CO}_3$, and $\text{Li}_2\text{CO}_3$, as shown in Fig. 5. The $\text{Na}_2\text{CO}_3$
contained in the green pellet liquefied at the melting point, and immediately reacted with α–
Al₂O₃ to form Na⁺–β/β'–Al₂O₃, preventing contact between the molten Na₂CO₃ and BASE.

Fig. 4. Na₂CO₃ stuck to the BASE surface after the VPC reaction.

Commercialization of the Na/NiCl₂ battery requires manufacturing cost to be reduced through
the reuse of surrounding powder and the reduction of the VPC process steps. Therefore,
research was conducted to optimize the reusable conditions and allowable range of the
surrounding powder in the VPC process, which has not been studied to date, and the properties
of the BASE and surrounding powder manufactured by reusing the surrounding powder in the
VPC process were analyzed.
Experimental methods

1. Preparation of the surrounding powder as a Na source

The surrounding powders used as Na sources in the VPC experiments were of three types. First, the Na$^+$–β$''$–Al$_2$O$_3$ powder was synthesized through a calcination process. Second, a mixture of raw material powders, here called the green mixture, was obtained by skipping the calcination process. The third type was the green pellets formed by pressing the green mixture.

As raw material powders, α–Al$_2$O$_3$ (99.99 %, High Purity Chemicals Co. Ltd., Japan), Na$_2$CO$_3$, and Li$_2$CO$_3$ for Li$_2$O as a stabilizer were used. For the experiment of reusing the surrounding powder, it contains 13 wt.% Na$_2$O, 0.4 wt.% Li$_2$O and 86.6 Al$_2$O$_3$ which is more than that applied in previous study [24,25].

The starting materials α–Al$_2$O$_3$, Na$_2$CO$_3$, and Li$_2$CO$_3$ were weighed according to the composition, and then put into a ball mill to be mixed and ground with methyl alcohol, which is a dispersion solvent, for 8 h. After mixing and grinding, the slurry was dried in oven at 90 °C for 24 h.

A portion of the dried powder (green mixture) was calcined at 1,200 °C for 2 h to synthesize it into Na$^+$–β$''$–Al$_2$O$_3$ powder. Another portion of the green mixture was prepared into two pellets of 3 g each by uniaxial press and placed on the top and bottom of the ZTA during VPC. The different types of surrounding powder and ZTA were put in an alumina crucible, as shown in Fig. 5, and then put into a box furnace to conduct VPC at 1,400 °C for 3 h. The ZTA, used as a precursor in the VPC process, is in the form of a disk of 25 mm diameter, 500 μm thickness and 1g weight, and was provided by the Research Institute of Science and Technology (RIST), Pohang.
2. VPC with green pellet

To reuse the surrounding powder after the 1st VPC, which is implemented using the green pellet as surrounding powder, the VPC was performed repeatedly with the used green pellet by replacing a new ZTA. The green pellet was reused up to three times.

Fig. 5. Schematic of the VPC using green pellet.

3. VPC for multiple production by layering

For multiple production of the BASE during VPC, the green pellets and precursor ZTAs were alternately stacked, and placed in an alumina crucible, the crucible lid was locked and sealed, and it was maintained at a temperature of 1,400 °C for 3 h, as shown in Fig. 6. In this experiment, a total of three ZTAs were used at once, and the possibility of multiple production was determined through analyzing the physical properties of the three BASEs manufactured by the VPC.

Fig. 6. Schematic of the VPC by multilayer stacking.

4. Properties measurement

X-ray diffraction (XRD) analysis was performed to determine the crystal formation and the crystal phase fraction of the specimen. The measurements were made on the BASEs with a diameter of 25 mm. The X-ray diffractometer was operated at a scan speed of 3 °·min⁻¹, 2θ range of (5–80)° with a power of 40 kV, 30 mA using Cu–K α–radiation. Calculation of the
relative fraction of the crystal phases from the line intensities of the well-resolved peaks was conducted using the following equations [26, 27]:

\[
\% \text{ of } \alpha = \frac{f(\alpha)}{f(\alpha) + f(\beta) + f(\beta'')} \times 100 \quad (1)
\]

\[
\% \text{ of } \beta = \frac{f(\beta)}{f(\alpha) + f(\beta) + f(\beta'')} \times 100 \quad (2)
\]

\[
\% \text{ of } \beta'' = \frac{f(\beta'')}{f(\alpha) + f(\beta) + f(\beta'')} \times 100 \quad (3)
\]

\[
f(\alpha) = \frac{1}{2} \left( I_{\alpha(104)} \times \frac{10}{9} + I_{\alpha(113)} \right) \quad (4)
\]

\[
f(\beta) = \frac{1}{3} \left( I_{\beta(102)} \times \frac{10}{3} + I_{\beta(206)} \times \frac{10}{3.5} + I_{\beta(107)} \times \frac{10}{5.5} \right) \quad (5)
\]

\[
f(\beta'') = \frac{1}{2} \left( I_{\beta''(1011)} \times \frac{10}{4} + I_{\beta''(2010)} \times \frac{10}{8} \right) \quad (6)
\]

where, \( I_{\alpha(104)} \) and \( I_{\alpha(113)} \) denote the X-ray intensities of the (104) and (113) planes of the \( \alpha \)-alumina phase, respectively; \( I_{\beta(102)}, I_{\beta(206)}, \) and \( I_{\beta(107)} \) represent the X-ray intensities of the (102), (206), and (107) planes of the \( \beta \)-alumina phase, respectively; and \( I_{\beta''(1011)} \) and \( I_{\beta''(2010)} \) indicate the X-ray intensities of the (1011) and (2010) planes of the \( \beta'' \)-alumina phase, respectively.

The microstructure analysis of BASEs after the VPC was performed using SEM (JEOL JSM-6308, Rigaku, Japan). In addition, the distribution state of sodium in BASEs was investigated using EDX. After polishing, the BASEs were heat-treated in an electric furnace at 1,350 °C for 30 min.

To measure the ion conductivity of the BASEs after the VPC, electrochemical impedance spectroscopy (EIS) measurement was performed using a complex impedance analyzer (Zahner, IM6, USA). Both sides of the sample were polished using SiC papers, and after applying Pt paste (Heraeus, Germany) with a diameter of 6 mm on both sides of the sample, it was dried in oven for 30 min, and heated in electric furnace to 1,200 °C to attach a Pt electrode. For EIS analysis, the frequency was set in the range (100 mHz to 3 MHz), and measured in the
temperature range (25 to 350) °C. The ion conductivity was calculated using the following formula:

\[ \sigma = \frac{L}{(R_m \times A)} \]

where, \( \sigma \) is the ion conductivity [S·cm\(^{-1}\)], \( L \) the membrane thickness [cm], \( R_m \) the membrane resistance [Ω], and \( A \) the electrode area [cm\(^2\)].

Qualitative and quantitative analysis of the elements constituting the green pellet with a wavelength-dispersive XRF (WD–XRF) was performed to analyze the residual Na content inside the green pellet after the VPC.
Results and discussion

1. Properties of the BASEs according to the type of surrounding powder

Fig. 7 shows the results of analyzing the XRD patterns of the BASEs after the VPC according to the three types of surrounding powder: Na\(^+–\beta/β"–Al_2O_3\) powder, green mixture, and green pellet.

This figure compares the phase analysis results for each surrounding powder. As a result of analyzing the XRD pattern, in all three BASEs, the main peak of α–Al_2O_3 at 2θ = (35.13 or 43.36)° was not observed, and the main peak of the β–Al_2O_3 was observed very weakly at 2θ = (19.92, 33.33 or 44.43)°, confirming that the ZTAs were mostly synthesized to the Na\(^+–\beta/β"–Al_2O_3\).

**Fig. 7.** XRD patterns of the BASEs after the VPC according to the type of surrounding powder.

Fig. 8 shows the microstructure of the BASEs prepared with the two different types of surrounding powder. Irrespective of the type of surrounding powder, it was confirmed that the BASE composites composed of the Na\(^+–\beta/β"–Al_2O_3\) and YSZ were well-formed, and no exaggerated grain growth occurred. Although subtle, the Na\(^+–\beta/β"–Al_2O_3\) grain sizes of BASE prepared using the Na\(^+–\beta/β"–Al_2O_3\) surrounding powder were found to be slightly smaller than those prepared using the green mixture.

**Fig. 8.** SEM images of the BASEs after the VPC according to the type of surrounding powder: (a) Na\(^+–\beta/β"–Al_2O_3\) powder, (b) green mixture.
To check the distribution and amount of Na\(^+\) ions inside the manufactured BASE that underwent VPC with green pellet, EDX analysis was performed after surface polishing, which is shown in Fig. 9. The red, green, and blue dots represent Na, Al, and O elements, respectively, and the Na\(^+\) ions can be seen to be well-distributed. It was confirmed that even if the surrounding powder is used in pressed form during the VPC process, the diffusion of Na\(^+\) ions is smooth.

**Fig. 9.** EDX analysis of the BASE after the VPC with green pellet as the surrounding powder.

To analyze the ionic conductivity of the BASEs prepared by the VPC process according to the three types of surrounding powder, the ionic conductivity was measured at temperatures ranging (150 to 350) °C by EIS, and Fig. 10 compares and analyzes the results.

The ionic conductivities of the BASEs produced by the VPC process using green mixtures and green pellets were found to be slightly higher than those using the Na–β"–Al\(_2\)O\(_3\) powder in all temperature ranges. This was attributed to the increased ionic conductivity due to the grain size of the Na\(^+\)–β/β"–Al\(_2\)O\(_3\) of BASE as shown in Fig. 8.

As a result, using a green mixture or green pellet was more effective for the ionic conductivity of the BASE than when using Na\(^+\)–β"–Al\(_2\)O\(_3\) powder as the surrounding powder. In particular, when green pellets were used, the phenomenon of the surrounding powder sticking to the BASE surface did not appear. Additionally, using green pellets has the advantage of reducing the VPC process costs by omitting the calcination process for producing the Na\(^+\)–β"–Al\(_2\)O\(_3\) powder.
Fig. 10. Ionic conductivity of the BASE after the VPC according to the type of surrounding powder in the temperature range (150–350) °C.

Table 1. Phase fraction and specific conductivity of the BASE at 200 °C according to the type of surrounding powder.

2. Properties of the BASEs manufactured through the reuse of green pellets

Fig. 11 and Fig. 12 show the results of the XRD pattern and EIS of the prepared BASEs after the VPC using the reused green pellets, respectively, while Table 2 shows the analysis of the phase fraction and their specific conductivity.

In the 1st VPC, which is implemented using green pellet as the surrounding powder, the BASE showed the highest Na$^+$–β"–Al$_2$O$_3$ phase fraction of 85.3 %, but in the 2nd VPC, which is implemented by reusing the surrounding powder used in the 1st VPC, the phase fraction was lowered to 84.3 %. In the 3rd VPC, which is implemented by reusing the surrounding powder used in the 2nd VPC, the Na$^+$–β"–Al$_2$O$_3$ phase fraction was further reduced to 84.0 %. Even in the 4th VPC, which is implemented by reusing the surrounding powder used in the 3rd VPC, the BASE consisted only of the Na$^+$–β– and β"–Al$_2$O$_3$ crystalline phase, where the Na$^+$–β"–Al$_2$O$_3$ phase fraction was 81.0 %. However, when the green pellet was reused beyond that, the α–Al$_2$O$_3$ phase remained in the BASE.

The specific conductivity of the BASEs was $2.1 \times 10^{-2}$ S·cm$^{-1}$ at 200 °C in the 1st VPC, and decreased to $0.9 \times 10^{-2}$ S·cm$^{-1}$ in the 4th VPC. This shows that the specific conductivity changes in proportion to the composition ratio of the Na$^+$–β"–Al$_2$O$_3$ phase.
During the phase transformation of the ZTA to the BASE, sodium released from the surrounding powder diffuses into the ZTA. In this process, the diffusion rate of sodium increases in proportion to the vapor pressure of the sodium surrounding the ZTA. The higher the diffusion rate, the greater the amount of sodium infiltrated into the ZTA, and thus the greater the Na–β"–Al₂O₃ phase fraction.

Fig. 13 shows the vapor pressure of the sodium released from the surrounding powder during the VPC process. The sodium vapor pressure of the green pellet was calculated using thermodynamic data (Table 3) and the Knudsen–Langmuir equation, and the sodium vapor pressure of the BASE was calculated with reference to Elrefaie and Smelzer [28].

Fig. 13. Vapor pressure of Na in the surrounding powder (raw material → Na⁺–β/β"–Al₂O₃).

**Table 3.** Thermodynamic properties of the Na–Al–O system.
Thermal decomposition of the Na$_2$CO$_3$ contained in the green pellet begins at 850 °C, and continues as the temperature increases, but at a very slow rate. The Na$_2$O formed by thermal decomposition gradually reacts with the α–Al$_2$O$_3$ starting at 900 °C, and changes the green pellet into the Na$^+$$\beta$$\beta''$–Al$_2$O$_3$ phase, so at 1,200 °C, all the surrounding powder is converted into the Na$^+$$\beta$$\beta''$–Al$_2$O$_3$.

The Na$_2$O remaining in the green pellet before the surrounding powder is completely converted to beta–alumina, which, having a relatively high sodium vapor pressure (Fig. 12), can promote the VPC reaction more effectively. Therefore, after the 1st VPC, the BASE shows the highest Na$^+$$\beta$$\beta''$–Al$_2$O$_3$ phase fraction.

To analyze the residual Na$_2$O content inside the green pellet according to the number of times of reuse of the green pellet, the components were analyzed qualitatively and quantitatively by WD−XRF. The components are composed of Al$_2$O$_3$ and Na$_2$O, and the Na$_2$O content in the starting state before VPC, and after the 1st, 2nd, 3rd, and 4th VPC, was measured at (13, 10.6, 9.76, 9.05, and 8.17) wt.%, respectively. Table 4 shows the Na$_2$O residual content according to the number of times of reuse of the green pellet. The Na$_2$O content in β–Al$_2$O$_3$ and β$''$–Al$_2$O$_3$ is calculated to be 5.2 wt.% and 10.8 wt.%, respectively, from the theoretical chemical formula. However, the two phases, β–Al$_2$O$_3$ and β$''$–Al$_2$O$_3$, are usually formed simultaneously in polycrystalline form, and the fraction of β$''$–Al$_2$O$_3$ actually shows the highest in the Na$_2$O content range of 8.5 - 8.9 wt.% [15-18]. As shown in Table 4, the Na$_2$O content of the surrounding powder used three times is maintained at 9.05 wt.%. This provided a favorable atmosphere for ZTA to undergo phase transition to β$''$–Al$_2$O$_3$, and as shown in Table 2, all specimens up to the 4h VPC formed a high beta phase of more than 80%. However, in the case of further reuse, the Na$_2$O content in the surrounding powder became insufficient to create β$''$–Al$_2$O$_3$ and β–Al$_2$O$_3$ phase rapidly increased and even α-Al$_2$O$_3$ phase appeared. This is evaluated to be able to set a reference point for the change in Na$_2$O content of the green pellets.
Table 4. Analysis of contents change in the surrounding powder after the VPC according to the reuse of green pellet

3. Properties of the BASE after the VPC for multiple production by layering

Fig. 14 and Fig. 15 show the results of the XRD pattern and EIS, respectively, of the prepared BASEs after VPC for multiple production by layering. Table 5 shows the analysis of the phase fractions and their specific conductivity.

The XRD patterns show that the three BASEs have the same pattern, and that the $\alpha$–$\text{Al}_2\text{O}_3$ phase in the BASE has been completely converted to $\text{Na}^+\text{--}\beta/\beta''\text{--Al}_2\text{O}_3$ phase. The ionic conductivities of the BASEs also show the same value in all measured temperature ranges, regardless of the location of the BASEs stacked in layers within the reactor during the VPC.

Additionally, as shown in Table 5, all three BASEs have very high $\text{Na}^+\text{--Al}_2\text{O}_3$ phase fraction. This is attributed to the free space inside the alumina reactor being reduced by stacking several BASEs in the alumina reactor, thereby increasing the vapor pressure of sodium in the reactor. Accordingly, it seems that as the sodium vapor pressure around the ZTA increased, the ZTA was more actively converted to the $\text{Na}^+\text{--Al}_2\text{O}_3$ phase.

After multiple production by layering, all three BASEs show the specific conductivity value of $1.7 \times 10^{-2}$ S·cm$^{-1}$. The conductivity of BASE is mainly affected by the phase fraction of the $\text{Na}^+\text{--Al}_2\text{O}_3$, but other factors, such as the grain size, grain arrangement, and orientation, which are influenced by the VPC reaction environment, also have a significant impact on the conductivity.

Fig. 14. XRD patterns of the BASEs after the VPC through multiple production by layering
**Fig. 15.** Specific conductivity of the BASEs within the temperature range (150–350) °C after the VPC through multiple production by layering

**Table 5.** Phase fraction and specific conductivity of the BASEs at 200 °C after the VPC by multiple production by layering.
Conclusions

In this study, we studied ways to reduce the manufacturing cost of thin disk-shaped Na⁺–β/β''–Al₂O₃ solid electrolyte (BASE), which is used as a core material in planar Na/NiCl₂ secondary batteries, using a vapor phase conversion process (VPC). Our approach focused on the Na⁺–β/β''–Al₂O₃ powder, a surrounding powder that is generally used in large quantities in the VPC process, but is discarded after just one use.

Two methods were studied through experiments. The first method was to use green pellets mixed with raw material powders, that is α–Al₂O₃, Na₂CO₃, and Li₂CO₃, instead of the Na⁺–β/β''–Al₂O₃ powder, as the surrounding powder. Through this, the calcination process necessary to synthesize the Na⁺–β/β''–Al₂O₃ powder could be omitted. During the VPC process, the problem of the Na₂CO₃ contained in the surrounding powder melting and sticking to the BASE surface could be solved by forming the surrounding powder into disk-shaped pellets. The ionic conductivity of the BASEs after the VPC with green pellets was no different from that of the conventional VPC using the Na⁺–β''–Al₂O₃ powder as the surrounding powder.

The second method was to reuse green pellets that had previously been used in the VPC. Since the number of reuses of green pellets is proportional to the amount of surrounding powder for the precursor ZTA, it was necessary to set a reference for the experimental conditions, so the weight ratio of the two materials was maintained at 3:1. Through the reuse experiment, the green pellet was reused three times, that is, one surrounding powder was used a total of four times; and after three times of reuse, the ionic conductivity of the BASE was maintained close to 10⁻² S·cm⁻¹.

To manufacture BASE in large quantities during the actual production process, multiple BASEs must be manufactured in one process. As an experiment for this purpose, the precursor ZTAs and the green pellets were stacked in several layers in a reactor, and the VPC reaction
was performed. As a result of the multiple production experiment by layering, all BASEs showed the same properties, which suggests that the multiple production method by layering can produce BASEs with the same properties.

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