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PAPER

Epoxy-reinforced ceramic sheet as a durable solid electrolyte for solid state Na-ion batteries

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In a conventional Na-ion battery system using liquid electrolyte, there are critical safety issues due to the instability of the liquid electrolyte. $Na_3Zr_2Si_2PO_{12}$ (NASICON) solid electrolyte is a material that is sufficient to replace a liquid electrolyte as it has high ionic conductivity and thermal and electrochemical stability. However, as there is a large interfacial resistance in the NASICON solid electrolyte powder, even when used in combination with a polymer electrolyte, the advantageous effects of ceramics are not easily exhibited. In this study, we propose a top-down method of combining a polymer with a ceramic in which an ion transport channel is previously formed. In this method, a NASICON solid electrolyte is partially sintered to form ion transport channels. Then the NASICON solid electrolyte pores are filled with an epoxy polymer to increase the strength of the epoxy-NASICON composite electrolyte. This method demonstrates the possibility of our composite electrolyte being used as a thin and strong film. As a result of our methods, the ionic conductivity and thermal and electrochemical stability of NASICON was maintained, while the physical strength was enhanced by approximately 2 times. In addition, a capacity of 120 mAh/g and stability of 20 cycles were confirmed in a half cell with a $Na_3V_2(PO_4)_3$ cathode and Na metal. This method proposes a new direction for research regarding composite electrolytes created using an oxide-based solid electrolyte.

1. Introduction

Rechargeable Na-ion batteries (NIBs) are rapidly emerging as a potential technology to replace lithium in the energy storage market.[1] NIBs have significant advantages because of the low-cost and abundant resources of Na as compared to lithium.[2] With the recent increase in renewable energy generation and large-scale energy storage system (ESS) demand, low-cost NIBs are promising systems.[3] Currently researched NIBs have several issues regarding their organic liquid electrolytes, including flammability and potential safety hazards in large-scale applications.[4] In view of this safety issue, Na-ion solid-state battery systems that do not use organic liquid electrolytes are considered to be a suitable solution, and making solid electrolytes is important in the future of batteries.[5]

In general, the solid electrolytes used to develop Na-ion solid state battery systems are based on inorganic solid materials;[6, 7] particularly, oxide-based materials that have high ionic conductivity and electrochemically, thermally stable are being studied.[8-10] Among oxide-based materials, Na-β-Alumina materials have been mainly studied. Because of its high ionic conductivity, it has been used for use in all-solid-state batteries until recently.[11] However, it has the disadvantage of being vulnerable to moisture. Another stable oxide-based material is $Na_3Zr_2Si_2PO_{12}$ (Na super ionic conductor, NASICON). NASICON solid electrolytes are the promising oxide-based Na-ion conducting material, with a high ionic conductivity of over 10^{-4} S/cm at room temperature and stable air and moisture.[12] NASICON ceramics are electrochemically stable up to 7 V, making it suitable for use in high voltage batteries. Owing to its stability advantages, efforts have been made to use NASICON in solid-state NIB systems. However, there remains a critical problem in the resistance between solid particle interfaces caused by the fragile and rigid nature of the oxide material itself, regardless of how high the pressure of the solid electrolyte powder is, making it difficult to utilize in a solid-state battery system.[13-16]

There have been numerous studies on composite electrolytes with polymer materials with the aim to counteract the solid-solid interface resistance of these oxide-based solid particles. Polymer materials have flexible physical properties and are therefore suitable to compensate for the disadvantages of oxide-based solid ceramic electrolytes. Table 1 summarizes the previous studies and current trends of ceramic-polymer composite electrolytes for use in NIBs.[17-24] In most of the studies that use Na-ion conducting ceramics, a composite electrolyte was prepared with the aim that the ceramic powder would fill the role of ion transport in the polymer electrolyte. If ion transfer through the ceramic is confirmed, it is possible to increase the ceramic ratio and expect a thermally and electrochemically stable composite. However, if there is no ion transfer through the ceramic, the ionic conductivity decreases

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as the proportion of ceramics increases.[17-25] According to a recent report, the ion conductivity in the abovementioned composite electrolyte exists primarily through the polymer electrolyte, and the ceramics contribution is negligible.[25] Therefore, the ceramic is used only as a filler of the polymer electrolyte, and as the ratio of the polymer electrolyte is still high, the thermal and electrochemical instability characteristics of the polymer remain. Above experiment are summarized in Figure 1.

The influence of the solid electrolyte is not readily seen when the oxide ceramic is in a powder state. Therefore, more research is required surrounding methods that aim to increase the ceramic proportion and enable ion transport through ceramics. In particular, for ion conduction through ceramics, the ion transport channel of the oxide-based solid electrolyte must be formed separately in the composite electrolyte.

In this study, we propose a top-down method of combining a polymer with a ceramic in which an ion transfer channel has been previously formed. This allows for the main ion transport channel to pass through the ceramic while the polymer material can be used to improve the physical properties of the solid electrolyte. Moreover, since the proportion of ceramic in the composite electrolyte occupies more than 50 wt%, a thermally and electrochemically stable solid electrolyte can be produced.

To confirm the possibility of a top-down composite electrolyte, we used a method of partially sintering a high porosity ceramic solid electrolyte and filling its internal pores with a polymer material to increase the physical strength. A NASICON ceramic solid electrolyte[11] was used as the oxide-based solid electrolyte, and epoxy-NASICON solid electrolyte pellets were prepared by filling the internal pores with an epoxy-resin polymer material[26], thereby confirming the possibility of using the electrolyte in an NIB. Through this method, the physical properties are expected to increase in strength owing to the use of epoxy-resin polymer materials, while the ion conduction effect can be transferred through the sintered NASICON solid ceramic to create a high stable solid ceramic electrolyte. As a result, the ionic conductivity becomes 1.45 × 10^{-4} S/cm, the thermal and electrochemical stability of NASICON is maintained, and the physical strength is enhanced by approximately 2 times more than that of the bare NASICON pellet. In addition, cell performance stability of 20 cycles were confirmed in a half-cell with a $Na_3V_2(PO_4)_3$ (NVP) cathode and Na metal. This method will suggest a new direction to the existing method for producing a composite electrolyte using an oxide-based solid electrolyte. It is expected that composite solid electrolytes may be applied to various battery systems by combining the oxide-based solid electrolyte and the polymer material.

2. Experimental

2.1 Synthesis of NASICON solid electrolyte ceramic

Precursor materials required for NASICON solid electrolyte powder synthesis were used as follows. Na_2HPO_4 (Sodium phosphate dibasic, ACS reagent, > 99%, Sigma-Aldrich Korea), SiO_2 (Silicon dioxide, >99.5%, Sigma-Aldrich Korea), and ZrO_2

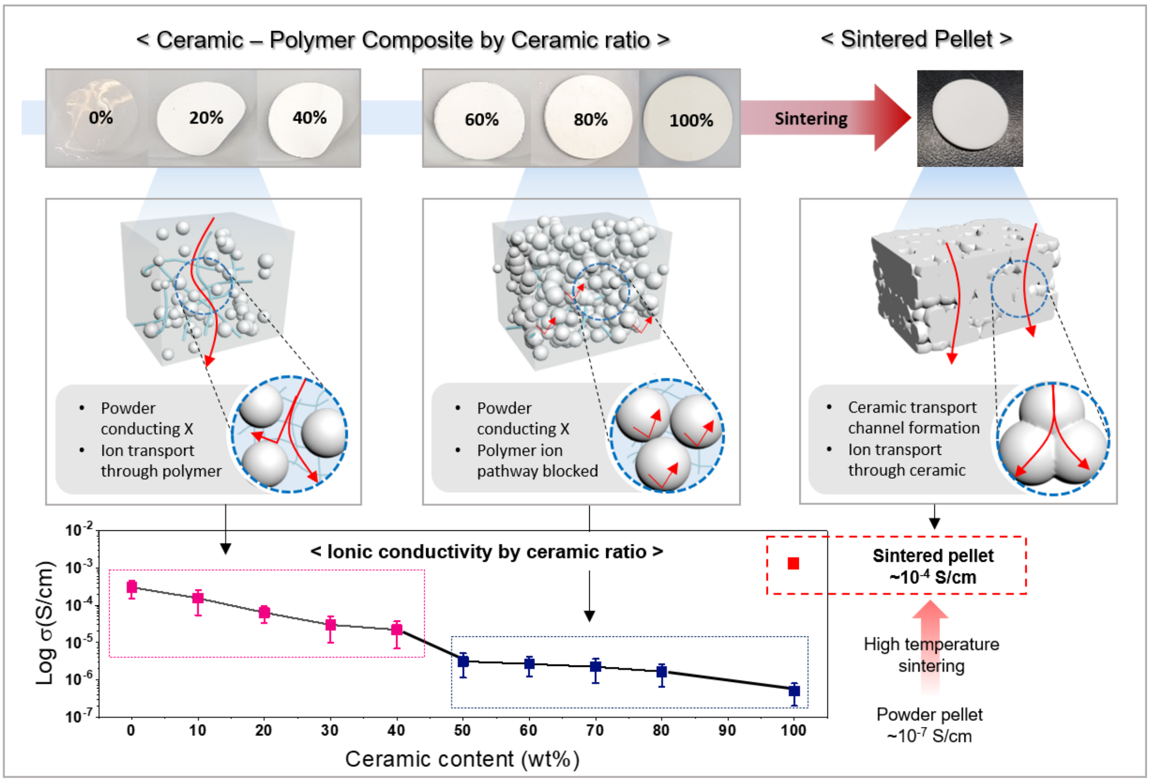

Fig. 1 Comparison of the ionic conductivity effect in different ceramic ratios in a ceramic-polymer composite state.

Composite electrolyte	Conductivity (S/cm)	Thickness (um)	Component ratio (Ceramic : Polymer)	Thermal stability	Ref
PEO-PVP/ NaF salt	1.1×10^{-7} (RT)	N/A	**15wt%** : 85wt%	N/A	[17]
EP-PEG/ SiO_2 Nanopowder	1.0×10^{-6} (RT)	N/A	**10wt%** : 90wt%	N/A	[18]
PEO-NaTFSI/ SiO_2 Nanopowder	1.0×10^{-5} (40℃)	~200	**10wt%** : 90wt%	< 150℃	[19]
PEO-$NaClO_4$/ TiO_2 Nanopowder	2.6×10^{-4} (60℃)	180-200	**5wt%** : 95wt%	N/A	[20]
PEO-NaFSI/ NASICON powder	4.4×10^{-5} (RT)	200-400	**40wt%** : 60wt%	< 150℃	[21]
PEO-NaTFSI/ $Na_{3.4}Zr_{1.8}Mg_{0.2}Si_2PO_{12}$	6.0×10^{-5} (30℃)	200-300	**50wt%** : 50wt%	< 237℃	[22]
PEO-$NaClO_4$/ SiO_2 powder	1.6×10^{-4} (60℃)	N/A	**5wt%** : 95wt%	N/A	[23]
PEO-$NaClO_4$/ $Na_3Zr_2Si_2PO_{12}$ powder	2.1×10^{-5} (RT)	~100	**25wt%** : 75wt%	N/A	[24]

Table 1 Complied research data and trends of ceramic-polymer composite electrolytes in Na-ion solid state batterie.

(Zirconium oxide, 99%, Sigma-Aldrich Korea) were purchased. These were dissolved in EtOH in accordance with NASICON stoichiometry, ball milled for 1 d, and then dried to obtain the precursor powder. Thereafter, the powder was cold pressed to form pellets and then sintered. The pellets were first sintered at 400 °C for 4 h, then 800 °C for 4 h, and finally at 1100 °C for 10 h. After synthesis, an X-ray diffraction (XRD) analysis verified that the NASICON crystal phases were formed (Supporting Figure S1).

2.2 Synthesis of epoxy-resin polymer solution and epoxy-NASICON composite

The epoxy-resin polymer was prepared as follows. Monomer bis (4-glycidyaloxyphenyl) propane and 1,3-phenylenediamine were dissolved in tetrahydrofuran (THF) at 1M and stirred for 1 h until dissolved completely. Each solution was then mixed at a volume ratio of 2:1 and stirred again for 1 h. The mixed solution was used as an epoxy-resin polymer solution.

After saturating the porous NASICON pellets with the epoxy-resin solution, they were maintained in a vacuum to allow for absorption into the internal pores. After repeating this process three times, the NASIOCN sample absorbing the epoxy polymer was heat-treated at 150 °C for 24 h. After this thermal polymerization sample, a brown epoxy-NASICON sample was obtained.

2.3 Physical properties and electrochemical analysis

The bending strength was calculated by a KS L 1591 three-point strength measurement and was measured by the Korea Institute of Ceramic Technology. For the three-point strength measurement, the bending strength of the sample was obtained by measuring the force when the sample breaks by applying an opposite force to the center point of the sample supported at 2 points. The formula for the three-point strength measurement is as follows:

$$\sigma = 3\mathrm{FL}/2\mathrm{bd}^2 \qquad (1)$$

where σ is the bending strength of the sample, F is the load (force) at the fracture point (N), L is the length of the support span, b is the sample width, and d is the thickness of the sample. In this strength measurement, all the pellet samples were tested in a 20 mm × 20 mm area, and the thickness was measured at 1.3 mm. The measurement speed was 0.5 mm/min. The breaking load at the time of measurement can be confirmed in the supporting Table S1.

A thermogravimetric analysis (TGA) was performed by adjusting the rate of temperature increase by 1 ℃/min from room temperature to 700 °C in an air atmosphere. The instrument used was a Q500 model from TA instruments.

Cyclic voltammetry (CV) was performed on the surface of the solid electrolyte pellets by contacting Na metal on one side and Pt sputter on the other, followed by the sus electrode. The scan rate was measured at 0.05 V/min from −1 V to 7 V. The measuring instrument was used the Bio-logic VSP-300 model.

The NASICON solid electrolyte material characterization was investigated through an XRD analysis using a Bruker D8 Advance X-ray diffractometer with a Cu Kα X-ray source. Measurements were recorded with a 2θ range of 10°–80°. Scanning electron microscope (SEM) images and an energy dispersive spectrometer (EDS) analysis of the films were taken using Verios 460, FEI and XFlash 6130, Bruker, respectively, operated at an accelerating voltage of 10 KV.

The porosity of the sintered NASICON pellet was measured using the Archimedes measurement method, where one calculates the proportion of internal pores by measuring the weight of the sample in the air and the weight of the sample after immersing it in water. The porosity is calculated by the following expression:

$$Porosity = \frac{W_3 - W_1}{W_3 - W_2} \times 100, \qquad (2)$$

where W_1 is the pristine weight of sample, W_2 is the sample weight in water, and W_3 is the sample weight containing water weight.

Electrochemical impedance spectroscopy (EIS) measurements were performed by Pt sputtering on both sides of the solid electrolyte pellets, and electrochemical characterization was done using SUS electrodes. Bio-logic VSP-300 models were electrochemically tested at a frequency range of 7 MHz to 100 MHz at 10 mV. Ionic conductivity was calculated with the following expression:

$$\sigma = \frac{l}{A} \times \frac{1}{R}, \tag{3}$$

where σ is the ionic conductivity (S/cm), l is the thickness of the sample (cm), A is the measuring area (cm), and R is total resistance (Ω).

2.4 Solid-state cell preparation method

For the cell test, the cathode material $Na_3V_2(PO_4)_3$ (NVP) was used. A cathode slurry mix of NVP active material, a super-P conductive agent, an ionic liquid electrolyte, and a polyvinylidene fluoride (PVDF) binder at a weight ratio of 70:10:10:10 was prepared. The ionic liquid electrolyte was prepared by mixing sodium trifluoromethanesulfonic (NaTFSI, sigma-Aldrich) salt and 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (Py14TFSI, sigma-Aldrich) ionic liquid at 1 M concentration. The prepared cathode slurry was coated on the surface of the solid electrolyte and then dried in vacuum oven for 2 hours.

For the anode, a UV curing polymer electrolyte layer was made between the Na metal and solid electrolyte. The UV curing polymer electrolyte was prepared by mixing trimethylolpropane ethoxylate triacrylate (ETPTA, Sigma-Aldrich), NaTFSI, and triethylene glycol dimethyl ether (TEGDME, Dae-jung) at a weight ratio of 45:15:40. Then, 2-hydroxy-2-methylpropiophenone was added and mixed as an initiator before use. The mixed solution was dropped on the surface of the solid electrolyte, and then covered with a release film made of polypropylene (PP) and cured by irradiating UV (365 nm) for 15 min.

Then, Na metal was placed on the surface of the UV curing polymer electrolyte, and the results of a cell test in which a Na metal/solid electrolyte/cathode was made was placed in a 2032-coin cell. All steps were processed in a glove box with less than 10 ppm for both oxygen and moisture. When manufacturing the bipolar stacked cell, a coin cell was prepared by putting Al foil between the two solid electrolyte cells.

The electrochemical cell test was performed using an automatic galvanostatic charge-discharge unit (WonATech. Co.) with a 2032-coin cell between 2.6 V and 3.8 V with 0.1 C-rate. All cell tests are performed in room temperature.

3. Result and Discussion

Previously, composite electrolytes intended for use in NIBs only used ceramic material as a ceramic filler for existing polymer electrolytes.[27-30] A ceramic filler, having approximately 20 wt% to 30 wt% of the total electrolyte ratio, was used to enhance the physical properties of the polymer electrolyte and to improve the ion transfer effect. Recently, research has been conducted to increase the ratio of ceramics in anticipation of the ion conducting effect of solid electrolyte powders with NASICON powder. Regarding the ceramic solid electrolyte, we expected that the polymer electrolyte would reduce the interfacial resistance between the solid ceramic powders. However, the proportion of the ceramic solid electrolyte was yet to be increased to 50 wt% or more, allowing the ceramic solid electrolyte powder to continue to operate as a ceramic filler.[31-33] Previous experiments were conducted to investigate why the ratio of ceramics could not be increased, and the results can be seen in Figure 1. We measured the ionic conductivity by mixing a polymer electrolyte and NASICON powder from 0% to 100% by weight ratio. A UV curing polymer electrolyte in Experiment part 4 was used as the polymer electrolyte. As a result of the experiment, when the ceramic ratio is under 40 wt%, the composite electrolyte generally showed a high ionic conductivity, which is due to the polymer electrolyte. However, as the proportion of ceramics increased, the ionic conductivity gradually decreased. According to a recent study, the increase in the proportion of ceramics does not have much effect on the ion transfer through the ceramic solid electrolyte, but rather, a phenomenon occurs in which conductivity is reduced owing to interference with ion conduction of the polymer electrolyte.[25] In particular, when the ceramic ratio increases by 50 wt% or more, a sharp drop in ion conductivity is observed. This means that there is little ion conduction between both the polymer-ceramic and the ceramic-ceramic in the composite electrolyte. Consequently, even if a ceramic-polymer composite electrolyte is fabricated, the disadvantages of the polymer electrolyte remain, including low thermal stability and low ion conductivity at room temperature.

Ultimately, a high temperature sintering process is required to ensure ion transfer through the oxide-based solid electrolyte. The high temperature sintering process is the simplest way to reduce the resistance between the ceramic powder interfaces. As seen in Figure 1, after high temperature sintering, the ceramic solid electrolyte forms a channel through which ions can transfer. The ionic conductivity, which was approximately 10^{-7} S/cm (measured by simply compressing the ceramic powder), rose to almost 10^{-3} S/cm after the sintering process. The ionic conductivity results measured by the EIS test can be confirmed in Supporting Figure S2. In this regard, it was assumed that the ceramic ionic conductivity was first obtained during sintering process. The study of such a composite electrolyte has been actively conducted in the field of Li ion solid electrolyte and there are many studies.[34-37] However, there is no research beyond the current level in the NIB field, and further research and development is needed.

Sintering an oxide-based solid electrolyte that has a hard and brittle characteristic can only be done in the form of hard pellets,

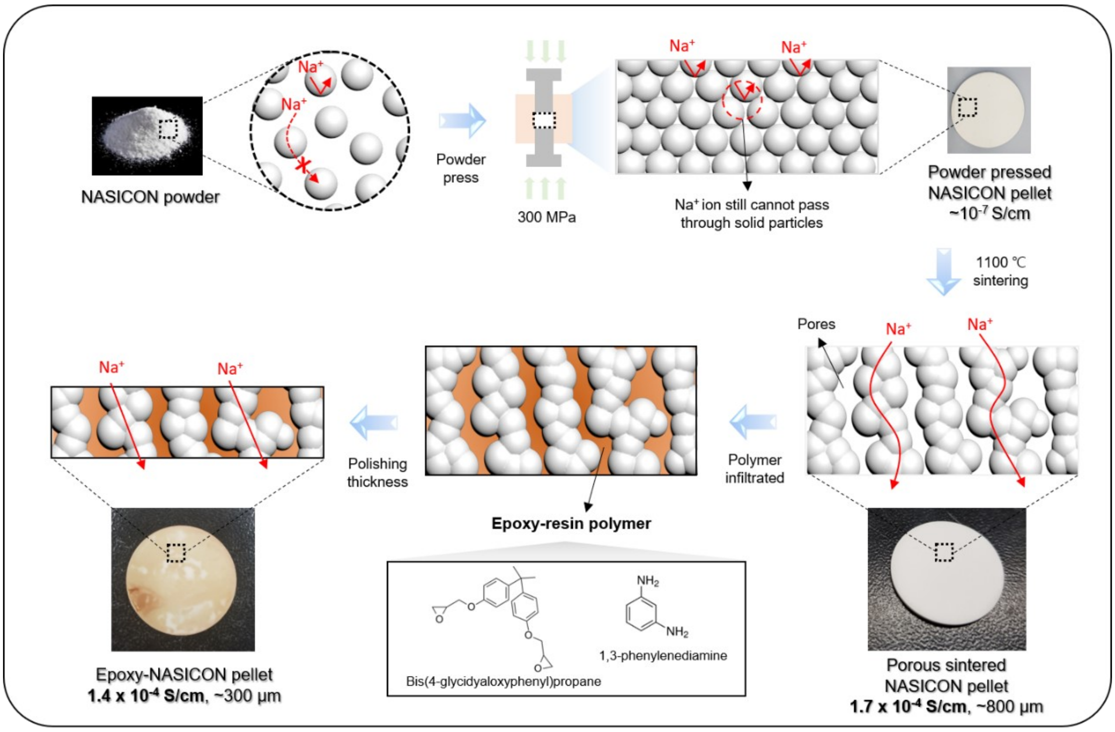

Fig. 2 Preparation of porous NASICON ceramic and epoxy-NASICON composite.

which are thick and easily broken.[38, 39] Therefore, although reducing the interfacial resistance results in a high ionic conductivity, it is difficult to manufacture a physically thin film form, causing limitations for application to actual battery systems. As Table 2 summarizes, the overall conductivity of the solid electrolyte is lower than that of the liquid electrolyte; however, the actual Na-ion conductivity is similar.[40-49] This is confirmed by the Na-ion transference number, which ranges from approximately 0.2 to 0.3 for most liquid electrolytes, whereas a solid electrolyte's transference number is 1.[38, 39, 50]

Table 2 The conductivity(σ) characteristics and resistance of NASICON solid electrolytes compared with those of conventional organic liquid electrolyte

	Total σ (mS/cm)	Na$^+$ ion σ (mS/cm)	Thickness (μm)	Total Ω (calculated)	Ref.
$NaPF_6$/ PC	8.0	5.8	~ 25	~ 0.21	[44,46]
$NaClO_4$/ PC	6.4	5.6	~ 25	~ 0.22	[44,46]
$NaCF_3SO_3$/ TEGDME	1.0	0.5	~ 25	~ 2.49	[46]
NaTDI/ PC	4.0	0.6	~ 25	~ 1.03	[47]
$NaPF_6$/ EC	6.8	2.0	~ 25	~ 0.62	[42]
$NaClO_4$/ DMC	5.0	1.0	~ 25	~ 1.24	[46]
NaTFSI/ EC, DMC	3.7	0.74	~ 25	~ 1.68	[45]
NASICON	0.78	0.78	~ 900	~ 230	[40]

When the usable thickness is compared with the separator thickness of the existing liquid electrolyte, the thickness of the solid electrolyte pellet is at least 30 times thicker than that of commercial separators. Due to this difference in thickness, the total resistance value is bound to be greatly different. Therefore, after sintering, sufficient strength must be reached to ensure that the thickness of the oxide-based solid electrolyte is as thin as possible.

To increase the strength of the ceramic pellets, we devised a method of combining polymers with sintered ceramics. Figure 2 shows the processes for sintering the ceramics and creating ceramic-polymer composite materials. The existing NASICON powder has an ionic conductivity of 10^{-7} S/cm, even when compressed at a pressure of 300 MPa. When the ceramic sample subjected to pressure is sintered for 10 h at over 1000 ℃ in a heat treatment furnace, the ceramic powders connect to each other to form a Na-ion conducting channel. The final sintering temperature is adjusted to intentionally increase the porosity of the ceramic pellet. Thus, the pores prepared can be polymerized after filling the polymer material in the monomer state. We filled the ceramic pellets in a liquid state monomer to maintain the vacuum state and ensure a sufficient fill of prepared polymer solution material into the pores of the ceramic. In this experiment, an epoxy-resin polymer was used to increase the physical strength. Epoxy-resin is not an ion-conducting polymer material; therefore, it is polished to reveal the surface of the solid electrolyte after polymerization. After this process, the Epoxy-NASICON composite electrolyte sample has a slight brown color under the influence of the polymer and can be reduced to 300 μm thickness by polishing, as shown in Figure 2.

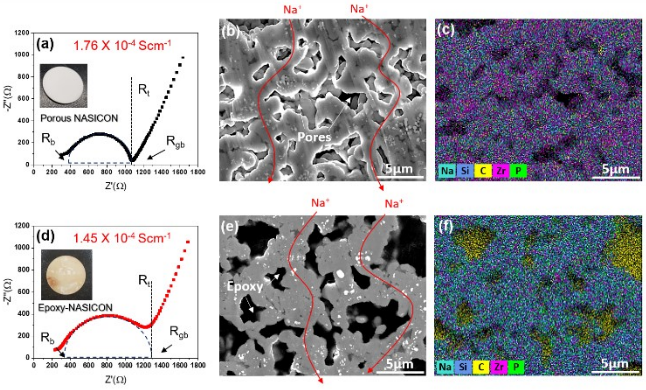

Fig. 3 (a) The ionic conductivity results of EIS measurement of porous NASICON pellets. (b) The sintered porous NASICON cross-section SEM image and (c) EDS result. (d) The ionic conductivity results through EIS measurement of epoxy-NASICON pellet. (e) The epoxy-NASICON composite electrolyte cross-section SEM image and (d) EDS results.

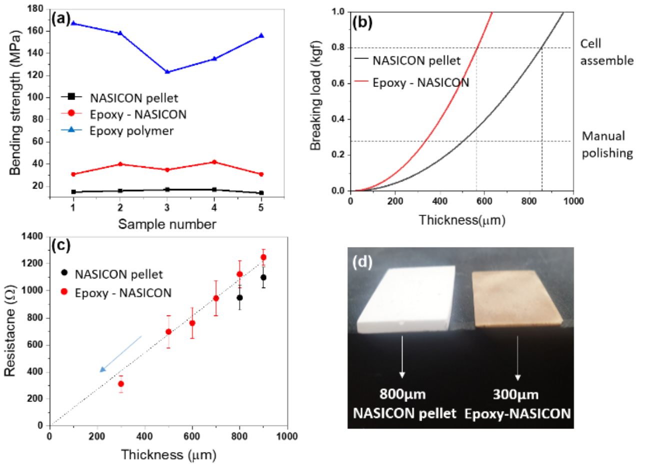

Fig. 4 (a) Bending strength test result of each NASICON pellet, Epoxy-NASICON, and Epoxy polymer. The average value of each test result is 15 MPa ± 2 MPa, 35 MPa ± 5 MPa, and 150 MPa ± 15 MPa, respectively. (b) Graph of solid electrolyte pellet strength based on the measured bending strength values. (c) Resistance value results for each solid electrolyte thickness. (d) Images of NASICON pellet and epoxy-NASICON pellet sample.

Porosity control during NASICON sintering, which is before the addition of epoxy polymer, can be adjusted by controlling the final sintering temperature, thereby creating a difference in porosity of the ceramic (Supporting Figure S3). When the final sintering temperature is 900 ℃, the sinterability of the NASICON powder starts to increase. However, the porosity was measured to be over 20%, and the ionic conductivity was under 10^{-7} S/cm, thereby demonstrating that the ion transfer channel formation has not been completely achieved. At a sintering temperature of 1000 ℃, the ionic conductivity of the NASICON pellets appears to increase rapidly. As shown in Supporting Figure S3, an ionic conductivity of 10^{-4} S/cm or greater appears at 1000 ℃. Therefore, it can be assumed that the ion transport channel was successfully formed through sintering. It can also be seen from the SEM cross-sectional image (Supporting Figure S4) that sufficient bonding was achieved between the NASICON powders. At a sintering temperature of 1000 ℃ or higher, the ionic conductivity increases as the temperature increases; however, when it exceeds 1100 ℃, the porosity decreases rapidly, making it unsuitable for composites with polymer materials. Therefore, our experiment was performed using NASICON pellets sintered at 1100 ℃, which was determined to be the optimum condition, with a porosity of approximately 10%.

Figures 3(a) and (d) show the results of ion conductivity through EIS measurements of the porous NASICON pellets and epoxy-NASICON pellets, respectively. The NASICON ceramics sintered at 1100 ℃ had an ionic conductivity of 1.76×10^{-4} S/cm. A cross-sectional SEM image of the NASICON pellet sintered at 1100 ℃ is shown in Figure 3(b). Here, the solid electrolyte secures the ion transfer channel after sintering, leaving pores to remain inside. When the epoxy polymer is added to the sample, the polymer material sufficiently fills the internal pores (Figure 3(e)). In the SEM image, it was confirmed that the empty space between the NASICON crystals was filled in with a black material, which was identified as a polymer material containing C through the EDS analysis shown in Figures 3(c) and (f). The detailed EDS analysis results for each component can be seen in Supporting Figure S4. Comparing the components of Na, Si, Zr, and P, which are all contained in NASICON, with the components of C, which are only contained in the Epoxy polymers, we can see that the Epoxy polymer is completely contained in the inner pores. In the same sample, Na-ions only move through the connected ceramics, which means that adding the epoxy polymers does not affect the ion conduction. The ionic conductivity after epoxy treated NASICON pellet is determined to be 1.45×10^{-4} S/cm. Therefore, epoxy polymer is not involved in the ion transport mechanism, so it can increase the physical strength while maintaining the existing ion conductivity.

The physical strength of the ceramic samples increased significantly after the epoxy polymer treatment. For physical strength measurement, a three-point bending strength measurement method was used, and each of the samples having a thickness of 1.3 mm in an area of 20 mm × 20 mm was measured. As seen in Figure 4(a), the NASICON ceramics have an average bending strength of 15 MPa (± 2 MPa), even when sintered at high temperature of 1260 ℃ with a higher density. Curing only the epoxy polymer creates an average bending strength of 150 MPa (± 15 MPa). Experimental measurements of each substance are in Supporting Table S1. The bending strengths of bare NASICON (15 MPa) and epoxy-NASICON pellets (35 MPa), shown in Figure 4(b), are calculated as the forces that can withstand the actual pellet area. When both materials are polymerized after filling with ceramic, the epoxy polymer materials connected to each other through the open pores inside the ceramic support the inside, thereby preventing the ceramic from breaking inside. The epoxy-NASICON sample after epoxy treatment has an average bending strength of 35 MPa (± 5 MPa). While manufacturing a coin cell, the minimum strength that the solid electrolyte can withstand is required. In the case of the coin cell produced in this study, at least 0.8 kgf must be sustained. When bare NASICON pellets were used, they were mostly available in thicknesses ranging from 800 μm to 900 μm. For calculations with a thickness of less than 600 μm, epoxy-NASICON was used, and for real experiments, a 500 µm thick sample is required. Epoxy-NASICON is expected to be used more in the future because it can be used in a thinner state than that of existing solid electrolytes that have the same physical properties. Based on this, the thickness of epoxy-NASICON was reduced, and the actual resistance is measured. Figure 4(c) shows that the resistance decreases in proportion to the thickness. Drawing a trendline based on the measured results for a minimum thickness of 120 µm ensures that the solid electrolyte resists less than 100 Ω. In the actual solid electrolyte sample in Figure 4 (d), we see that the existing 800–900 µm thick NASICON sample can reduce its thickness up to 300 µm. If a solid electrolyte with a small thickness and the same strength and resistance value can be developed, its applicability will undoubtedly increase. The possible enhancements of the epoxy-NASICON composite's physical properties can be predicted by the rule of mixture equation, which is used to calculate the properties of a mixture of different physical properties.[51] Supporting Figure S4 shows the actual strength as determined by the rule of mixture equation. The maximum value that can be predicted by a general equation can be obtained by the following expression:

$$E_{composite} = fE_{epoxy} + (1-f)E_{NASICON}, \qquad (3)$$

Where f is the volume fraction of the epoxy polymer, E_{epoxy} is the physical property (bending strength) of the epoxy polymer, $E_{NASICON}$ is the physical property of the NASICON ceramics, and $E_{composite}$ is the physical property of the epoxy-NASICON composite sample.

Additionally, the minimum predictable value can be obtained by the following expression:

$$E_{composite} = \left(\frac{f}{E_{epoxy}} + \frac{1-f}{E_{NASICON}}\right)^{-1}. \qquad (4)$$

The expected values in Equation (4) can be estimated from the maximum and minimum values according to the direction of the force applied to the material when there are no internal pores in the composite material and when there is a seamless connection. Regarding our developed epoxy-NASICON sample, shown in Supporting Figure S4(a), the ceramic electrolyte is sintered, which causes the ceramics to be seamlessly connected to each other. The inside of the ceramic is filled with epoxy polymer material without any remaining pores and polymerized without breaks, which allows the actual value to almost reach the expected maximum value.

The properties of the resulting epoxy-NASICON sample can be seen in Figure 5. Note that the NASICON ceramics are stable up to 700 ℃, and epoxy polymers are stable up to 400 ℃ after curing, as confirmed by a TGA experiment (Figure 5(a)). Since each material is stable at 400 °C, the epoxy-NASICON sample is stable until 400 °C. CV was conducted to confirm the electrochemical stability of the sample. In Figure 5(b), epoxy-NASICON with Na metal showed no side reaction up to 7 V, except for the plating/stripping of Na metal near 0 V. Therefore, we believe that both the NASICON ceramic and epoxy polymers are electrochemically stable, and no other chemical reaction occur in the composite process.

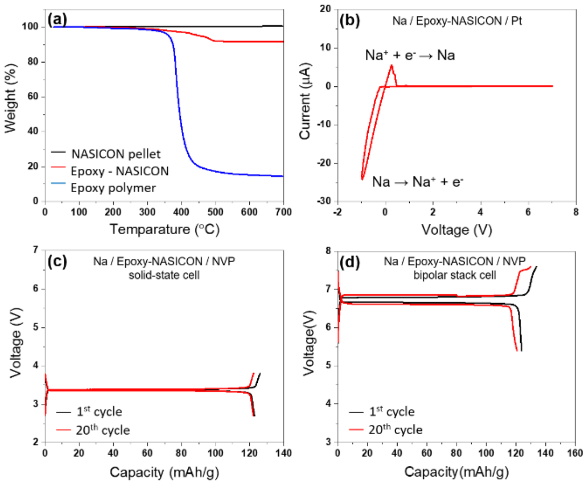

Fig. 5 (a) Thermogravimetric analysis data of NASICON ceramic, epoxy-NASICON composite, and epoxy polymer. (b) Cyclic voltammetry of Na metal/epoxy-NASICON/Pt state cell. Scan rate was 0.05 V/min from -1 V to 7 V. (c) Cell performance graph of Na/epoxy-NASICON/$Na_3V_2(PO_4)_3$ half-cell. The charge/discharge was conducted with 0.1 C-rate current at room temperature. (d) Cell performance graph of bipolar stacked cell. The charge/discharge was conducted with 0.1 C-rate current at room temperature.

To confirm the possibility of using an epoxy-NASICON electrolyte for a solid-state battery, a cell test was carried out by attaching positive and negative electrodes to our composite. As the positive and negative electrode materials are currently used as solid active materials, the use of an electrolyte as a solid material causes a contact resistance problem again. In addition, it is difficult to confirm the cycle performance because it is difficult to compensate for the volume change of the active material generated during the charging and discharging of the solid electrolyte. In this experiment, the cell design was conducted as follows to confirm the applicability of epoxy-NASICON as a solid electrolyte. A cathode part was made by mixing 10 wt% of ionic liquid electrolyte into a total cathode part in order to reduce the interfacial resistance between the cathode active material and solid electrolyte. Meanwhile, for the anode part, Na metal was added to the UV curing polymer electrolyte layer between the solid electrolyte and the Na metal to minimize contact resistance. As there is no liquid electrolyte leaked, ions are able to move through the solid electrolyte channel during the charge and discharge process. When the half-cell of NVP cathode material and Na metal were manufactured and charged and discharged at a rate of 0.1 C, a capacity of 120 mAh/g and 20 cycles were stably completed. Reproducibility confirmation through repeated experiments can be confirmed through Supporting Figure S6. The charge/discharge graph is shown in Figure 5(c). This capacity is sufficient even when using a conventional liquid electrolyte, and the coulomb efficiency is also relatively stable at 98%. To date, it has been difficult to manufacture a solid electrolyte up to approximately 25 µm, which is the separator thickness used

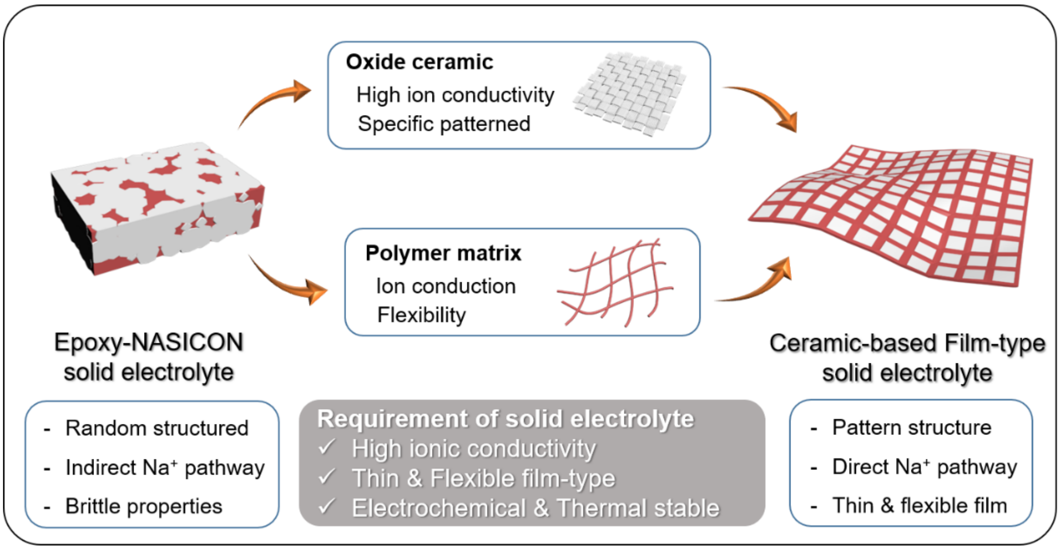

Fig. 6 Future enhancements of oxide ceramic based composite electrolytes.

for existing liquid electrolytes. Therefore, if the above cell performance can be reached with a solid electrolyte of the current thickness, it is expected to be applicable in a wide range of solid electrolytes. In addition, if a battery system using solid electrolyte is manufactured, we are able to make a bipolar stacking cell as there is no leakage inside the solid electrolyte cell. If a high voltage battery can be made through a bipolar stack in a single cell, then it is advantageous for use in high energy storage devices. In this study, a 7 V class coin cell was fabricated by stacking double solid-state cells in a single coin cell. The epoxy-NASICON solid electrolyte can be applied to the bipolar stack cells because it is thin enough to put two or more solid electrolytes in a single coin cell. The bipolar stacked coin cell experiment results include 6.8 V charge and 6.6 V discharge graphs that show stable operation at a capacity of 120 mAh/g for up to 10 cycles (Supporting Figure S7). The charge/discharge graph of bipolar stacked cell is shown in Figure 5(d). Based on these results, we see that the cell performance is the ion-transferring role of our epoxy-NASICON composite electrolyte.

To manufacture a thin and strong solid electrolyte, high-strength polymers, such as epoxy-resin, were inserted into the pores of sintered NASICON ceramics, and the possibility of increasing the strength while maintaining the electrochemical properties was confirmed. From our data, we confirmed the possibility of using our composite in a solid-state battery cell. Nevertheless, current methods still have limitations regarding thickness, which should be below 20 μm, i.e., the thickness of the conventional NIB system. According to the reference of the paper, the basic physical characteristics that require the current conventional battery separator are >1000kg cm^{-1} tensile strength and >98.06 MPa bending strength.[52] To achieve this figure, our solid electrolyte system is still far below the bending strength. Therefore, further research is necessary to develop thinner, more flexible solid electrolytes while maintaining the current approach. The direction for future studies of solid electrolytes using ceramics is shown in Figure 6. Note that the sintering process is essential to secure ion transfer paths using ceramic solid electrolytes. Currently, the sintering process causes NASICON powders to connect randomly and appear only as a solid pellet. It would be ideal if the ceramic could be sintered in a specific pattern that is physically flexible and optimized for ion transfer. The best pattern for ion transfer is the vertical ceramic in the composite electrolyte. Meanwhile, if the bond with the polymer material is good and sintering is possible with a regular area, a film-type composite electrolyte can be created (Figure 6). Therefore, a new method of making a ceramic of a specific pattern using 3D printing or a sacrificial template is being studied.[53, 54] In addition, the polymer material used to enhance the physical characteristics should have a high Na-ion conductivity, thereby maximizing the ion transfer effect of the solid electrolyte in the future, making it possible to manufacture a thin and flexible film-type solid electrolyte capable of ion transfer by sintering the ceramic in this way. We expect that this film-type oxide-based solid electrolyte will be applied in the NIB field and used as a safe energy storage device.

4. Conclusions

In a ceramic-polymer composite electrolyte, because ion transfer is difficult with ceramic powder, an ion transport channel through the ceramic must be previously formed to realize the ion conducting ceramic effect. We proposed a top-down method composite, in which a polymer on a ceramic has a pre-formed ion transport channel. To confirm the possibility of a top-down composite electrolyte, we used a method of partial sintering on a NASICON ceramic with high porosity and filled its internal pores with an epoxy polymer to increase physical strength. By controlling the porosity of the epoxy-NASICON pellet to approximately 10%, we accomplished more than twice the strength compared with that of the existing NASICON pellet. The electrochemical stability was observed up to 7 V, which was confirmed via CV analysis, and thermal stability was observed up to approximately 400 ℃. The ionic conductivity was measured to be 1.45×10^{-4} S/cm at room temperature, and the thickness could be reduced to 300 μm. To see the possible applications of this epoxy-NASICON solid electrolyte, a half-cell was fabricated with an Na metal and NVP cathode. The cell was tested and stably operated for more than 20 cycles at a capacity of 120 mAh/g at 0.1 C rate. Based on this, we confirmed that a solid electrolyte can be sufficiently produced by pre-forming the ion transport channel of the ceramic and combining it with a polymer. Nevertheless, with the current sintering method, there are limitations in creating the ion transport channels and composite electrolyte. Further research is necessary to make ceramics with an intended pattern, rather than the formation of random ion transport channels. By creating a ceramic with a physically flexible pattern and an easy form for ion transfer, it is expected that a composite electrolyte in the form of a flexible film-type polymer composite can be produced. This research will facilitate the study of composite electrolytes that utilize oxide-based solid electrolytes and further contribute to the development of Na-ion solid state batteries.

Conflicts of interest

There are no conflicts to declare.

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Table of contents entry

NASICON ceramic electrolyte are pre-formed with ionic conduction channel through sintering process and Epoxy-resin polymer material infiltrate inside of NASICON ceramic pores. This method maintaining ionic conductivity of ceramic electrolyte and can fabricate thin sheet type solid electrolyte.