

Optimization of Sc^{3+} Ion Conduction in NASICON Type Solid Electrolytes

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Various types of trivalent Sc^{3+} cation conducting solid electrolytes of the $(\text{Sc}_{1-x}\text{Al}_x)_{1/3}\text{Zr}_2(\text{PO}_4)_3$ ($0 \leq x \leq 0.6$), the $\text{Sc}_{1/3}(\text{Zr}_{1-y}\text{Hf}_y)_2(\text{PO}_4)_3$ ($0 \leq y \leq 1$) and the $(\text{Sc}_{0.8}\text{Y}_{0.2})_{1/3}\text{Zr}_2(\text{PO}_4)_3$ solid solutions were prepared and the Sc^{3+} ion conducting properties were compared. The optimum Sc^{3+} ion conductivity in NASICON type solid electrolytes was successfully obtained for the $(\text{Sc}_{0.8}\text{Al}_{0.2})_{1/3}\text{Zr}_2(\text{PO}_4)_3$ and the $\text{Sc}_{1/3}(\text{Zr}_{0.8}\text{Hf}_{0.2})_2(\text{PO}_4)_3$ solids, holding almost the equivalent NASICON crystal lattice size, and the optimization of the Sc^{3+} ion conduction in NASICON structure was realized.

For the realization of the trivalent cation migration in solids, it is necessary to select the suitable structure for ion migration, which contains higher valent cations than trivalent state and possesses the large ion conducting pathway. By bonding the higher valency cations to counter oxide anions with a strong electrostatic interaction, the interaction between the conducting trivalent cation and constituent oxide anions considerably reduces. Recently, we have newly developed the trivalent Sc^{3+} cation conducting solid electrolyte $(\text{Sc}_{1/3}\text{Zr}_2(\text{PO}_4)_3)^1$ with NASICON (Na Super Ionic CONductor) type structure. The $\text{Sc}_{1/3}\text{Zr}_2(\text{PO}_4)_3$ solid contains two kinds of high valency cations such as tetravalent Zr^{4+} and pentavalent P^{5+} , and the lattice structure holds the three-dimensional network suitable for ion conduction. We have also clarified a clear relationship between the trivalent cation conductivity and the lattice size of $\text{R}_{1/3}\text{Zr}_2(\text{PO}_4)_3$ (R : Rare Earths).^{1,2} As reducing the R^{3+} radius, the lattice contracts and the trivalent conductivity enhances. The $\text{Sc}_{1/3}\text{Zr}_2(\text{PO}_4)_3$ solid, which contains the smallest trivalent cation among R^{3+} , shows the highest trivalent cation conductivity because the suitable conducting R^{3+} size for the lattice volume (A ratio³) in NASICON type structure is achieved. However, it is still unclear whether the lattice size obtained for $\text{Sc}_{1/3}\text{Zr}_2(\text{PO}_4)_3$ is an optimum one for the conducting trivalent Sc^{3+} ion in the NASICON type structure or not. In order to obtain the corresponding lattice size precisely, one of advantageous methods is to prepare the solid solutions in which the lattice size can be intentionally modified.

In this letter, we prepared various types of solid solution, $(\text{Sc}_{1-x}\text{Al}_x)_{1/3}\text{Zr}_2(\text{PO}_4)_3$ ($0 \leq x \leq 0.6$), $\text{Sc}_{1/3}(\text{Zr}_{1-y}\text{Hf}_y)_2(\text{PO}_4)_3$ ($0 \leq y \leq 1$), and $(\text{Sc}_{0.8}\text{Y}_{0.2})_{1/3}\text{Zr}_2(\text{PO}_4)_3$, in order to clarify the optimum lattice size for Sc^{3+} ion conduction and to maximize the trivalent Sc^{3+} ion conductivity in the NASICON type structure.

$(\text{Sc}_{1-x}\text{Al}_x)_{1/3}\text{Zr}_2(\text{PO}_4)_3$ and $(\text{Sc}_{0.8}\text{Y}_{0.2})_{1/3}\text{Zr}_2(\text{PO}_4)_3$ solid solutions were prepared by a sol-gel method from reagent grade of Sc_2O_3 (99.9%), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99.9%), Y_2O_3 (99.9%), $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (99%), and $(\text{NH}_4)_2\text{HPO}_4$ (99%). A stoichiometric mixture of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ or Y_2O_3 , and Sc_2O_3 was dissolved in 3% HNO_3 solution, then $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ was dissolved in nitric acid solution afterwards. By dropping $(\text{NH}_4)_2\text{HPO}_4$ solution (3%) into the HNO_3 solution, white pre-

cipitates were obtained. After heating the solution at 75 °C for 24 h, water was vaporized at 130 °C for 6 h and white powder remained was dried at 300 °C for 6 h. The powder obtained was pelletized and sintered at 850 °C for 24 h. The $\text{Sc}_{1/3}(\text{Zr}_{1-y}\text{Hf}_y)_2(\text{PO}_4)_3$ solid was also prepared by the similar sol-gel method using high purity HfCl_4 (99.99%). The characterization of the solid solutions was done by X-ray powder diffraction using $\text{Cu K}\alpha$ radiation (M18XHF, Mac Science). The data were collected by a step-scanning method for 2θ range between 10 and 70° with a step width 0.04° and a scan speed of 10°/min. Pt sputtered layer was prepared on both center surface of the sintered pellet. Electrical conductivity was measured by a complex impedance method in the frequency range from 20 Hz to 1 MHz (Precision LCR meter 8284A, Hewlett Packard). In order to identify the conducting ion species in solids, dc electrolysis was performed at 800 °C for 200 h by applying a dc voltage of 3 V between the Pt electrodes.

The XRD patterns of all samples prepared were the same profile as those of pure $\text{Sc}_{1/3}\text{Zr}_2(\text{PO}_4)_3$, and the peak angle of $(\text{Sc}_{1-x}\text{Al}_x)_{1/3}\text{Zr}_2(\text{PO}_4)_3$ ($0 \leq x < 1$) and $\text{Sc}_{1/3}(\text{Zr}_{1-y}\text{Hf}_y)_2(\text{PO}_4)_3$ ($0 \leq y \leq 1$) in which the Sc^{3+} (ionic radius: 0.0885 nm)⁴ or Zr^{4+} (0.086 nm)⁴ were substituted for smaller Al^{3+} (0.0675 nm)⁴ or Hf^{4+} (0.085 nm)⁴, respectively, shifted to higher angle. In contrast, the peaks of $(\text{Sc}_{0.8}\text{Y}_{0.2})_{1/3}\text{Zr}_2(\text{PO}_4)_3$ where Sc site is partially replaced by Y^{3+} (0.104 nm)⁴ was shifted to lower. These results clearly indicate that all samples obtained were the solid solutions and the lattice size of $(\text{Sc}_{1-x}\text{Al}_x)_{1/3}\text{Zr}_2(\text{PO}_4)_3$ and $\text{Sc}_{1/3}(\text{Zr}_{1-y}\text{Hf}_y)_2(\text{PO}_4)_3$ reduces and that of $(\text{Sc}_{0.8}\text{Y}_{0.2})_{1/3}\text{Zr}_2(\text{PO}_4)_3$

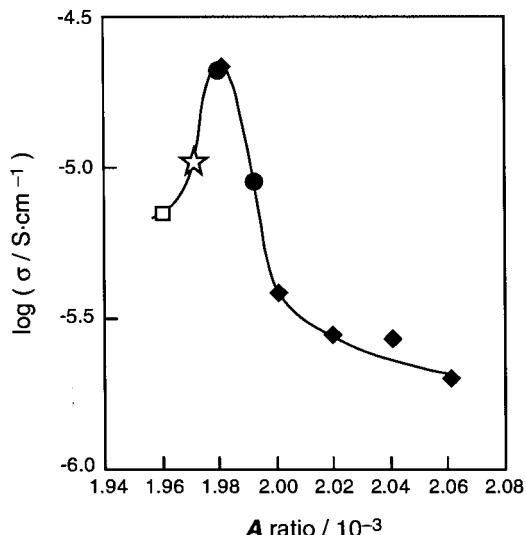


Figure 1. The A ratio dependencies of the electrical conductivity for the $\text{Sc}_{1/3}\text{Zr}_2(\text{PO}_4)_3$ (\star), the $(\text{Sc}_{1-x}\text{Al}_x)_{1/3}\text{Zr}_2(\text{PO}_4)_3$ (\bullet), the $\text{Sc}_{1/3}(\text{Zr}_{1-y}\text{Hf}_y)_2(\text{PO}_4)_3$ (\blacklozenge), and the $(\text{Sc}_{0.8}\text{Y}_{0.2})_{1/3}\text{Zr}_2(\text{PO}_4)_3$ (\square) solid solutions at 600 °C.

increases.

Figure 1 shows the A ratio dependencies of the trivalent ion conductivities for the $(\text{Sc}_{1-x}\text{Al}_x)_{1/3}\text{Zr}_2(\text{PO}_4)_3$, the $\text{Sc}_{1/3}(\text{Zr}_{1-y}\text{Hf}_y)_2(\text{PO}_4)_3$ and the $(\text{Sc}_{0.8}\text{Y}_{0.2})_{1/3}\text{Zr}_2(\text{PO}_4)_3$ solid solutions. While the conductivity increased with the A ratio up to 1.98×10^{-3} , the conductivity reduced with further increase of the A ratio. The maximum conductivity of $2.18 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ was obtained for $\text{Sc}_{1/3}(\text{Zr}_{0.8}\text{Hf}_{0.2})_2(\text{PO}_4)_3$ (A ratio: 1.98×10^{-3}) which was about two times as high as that ($1.07 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$) of pure $\text{Sc}_{1/3}\text{Zr}_2(\text{PO}_4)_3$ (A ratio: 1.97×10^{-3}).¹

In order to identify the conducting ion species in the solid solutions, the dc electrolysis of $\text{Sc}_{1/3}(\text{Zr}_{0.8}\text{Hf}_{0.2})_2(\text{PO}_4)_3$ was performed by applying a dc voltage of 3 V for 200 h. The ball shape deposits were recognized at the cathodic surface after the electrolysis and the amount of elements in the deposit were tabulated in Table 1. The Sc amount in the deposits was found to increase ca. 9.6 times as high as in the bulk before the dc electrolysis. The result explicitly means that the predominant conducting species in the solid solution is trivalent Sc^{3+} ions neither electron nor oxide anion similar to the case for pure $\text{Sc}_{1/3}\text{Zr}_2(\text{PO}_4)_3$.⁵

Table 1. The EPMA results for the bulk before electrolysis and for the deposit at the cathodic surface after the dc electrolysis of $\text{Sc}_{1/3}(\text{Zr}_{0.8}\text{Hf}_{0.2})_2(\text{PO}_4)_3$

Element	Amount (atomic %)	
	before electrolysis	after electrolysis
Sc	6.6	63.7
Zr	35.6	15.4
Hf	8.3	3.3
P	49.5	17.6

In conclusion, the enhancement of the trivalent cationic conductivity in the NASICON type structure was achieved by adjusting the lattice size with forming solid solutions. The Sc^{3+} ion conductivity was successfully improved ca. 2 times as high as that of pure $\text{Sc}_{1/3}\text{Zr}_2(\text{PO}_4)_3$ and the optimization of the Sc^{3+} ion conduction in NASICON type structure is successfully realized for both the $(\text{Sc}_{0.8}\text{Al}_{0.2})_{1/3}\text{Zr}_2(\text{PO}_4)_3$ and the $\text{Sc}_{1/3}(\text{Zr}_{0.8}\text{Hf}_{0.2})_2(\text{PO}_4)_3$ solid solutions.

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References and Notes

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- 2 S. Tamura, N. Imanaka, and G. Adachi, *Solid State Ionics*, **136-137**, 423 (2000).
- 3 A ratio is denoted as $(R^{3+} \text{ volume} / \text{lattice volume}) (R: \text{Rare Earths})$. The A ratio of $\text{R}_{1/3}\text{Zr}_2(\text{PO}_4)_3$ decreases with reducing the R^{3+} radius, and $\text{Sc}_{1/3}\text{Zr}_2(\text{PO}_4)_3$ has the smallest A ratio (1.97×10^{-3}) among the $\text{R}_{1/3}\text{Zr}_2(\text{PO}_4)_3$ series.
- 4 R. D. Shannon, *Acta. Cryst.*, **A32**, 751 (1976).
- 5 The oxygen partial pressure dependencies of the conductivity for $\text{Sc}_{1/3}(\text{Zr}_{0.8}\text{Hf}_{0.2})_2(\text{PO}_4)_3$ and $(\text{Sc}_{0.8}\text{Al}_{0.2})_{1/3}\text{Zr}_2(\text{PO}_4)_3$ were examined and the conductivity was found to be a constant in a wide oxygen pressure region between 10^{-12} Pa and 10^5 Pa , indicating that neither electron nor hole conduction appears in both solid solutions. From the measurement of the time dependencies of the dc to ac conductivity ratio (σ_{dc}/σ_{ac}), an abrupt decrease in the ratio was similarly observed in both helium (P_{O_2} : 4 Pa) and oxygen (P_{O_2} : 10^5 Pa) atmosphere. The phenomena explicitly indicate that oxide anion is not a conducting species in the solids.