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New trivalent rare earth ion (La, Nd, Gd) conducting solid electrolytes

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Abstract

New trivalent rare earth ion conducting $(R_xZr_{1-x})_{4/(4-x)}Nb(PO_4)_3$ (R: La, Nd, Gd) solid electrolytes based on the NASICON type structure, which have a three-dimensional network structure suitable for the R^{3+} ion conduction, were prepared and their ion conducting properties in their solids were investigated. The most suitable conducting path size for the R^{3+} ion conduction in the solids was identified from the relationship between the mobile ion size and the lattice volume. The typical ion conductivity of the rare earth phosphates was found to be in the order of 10^{-4} S cm^{-1} at 600 °C and the highest ion conductivity among the $(R_xZr_{1-x})_{4/(4-x)}Nb(PO_4)_3$ phosphate series was obtained for R = Nd. The conducting species in the $(Nd_xZr_{1-x})_{4/(4-x)}Nb(PO_4)_3$ solid electrolyte was identified to be the trivalent Nd^{3+} ion by the AC conductivity measurements in various oxygen partial pressures and also by the DC electrolysis.

Keywords: Trivalent ion; Rare earths; NASICON type phosphate

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1. Introduction

Solid electrolyte is one of many functional materials practically applied in industrial fields [1,2]. It has the unique characteristics of conducting only a single ion species in solids macroscopically with accompanying electric charge and has attracted a significant attention because of the promising application in various electrochemical devices such as all solid-state rechargeable batteries and chemical gas sensors. In the solid electrolyte field, a number of mono or divalent ions have been known to migrate in solids and some of them have been already commercialized as lithium batteries for heart pacemakers and oxygen sensors for vehicle emission control [3,4]. In contrast, trivalent cations have been regarded to be extremely difficult to conduct in solids due to their high electrostatic interaction with surrounding anions comprising the framework of structure. For the purpose of realizing a pure trivalent ion conduction, it is necessary to strictly select the structure suitable for ion conduction and in addition, to reduce the above interaction by containing cations with a valency higher than the conducting trivalent ion in the structure.

As pure trivalent cation conductors, $M_2(WO_4)_3$ (M = Al, Sc, Y, Er–Lu) tungstate series with the quasi-layered $Sc_2(WO_4)_3$ type structure [5–7] and $R_{1/3}Zr_2(PO_4)_3$ (R = Sc, Y, Eu–Lu) with the three-dimensional NASICON type structure [8–10] have been developed since 1995. However, their trivalent ion conductivities were still lower than those of mono- or divalent ions. Furthermore, the migrating ion species in these solids were limited to Al^{3+} ion and also some rare earth ions with small ionic radius.

From the practical view points, the further enhancement of the trivalent ion conductivity and the increase of the number of the conducting trivalent ion species are sought. While many rare earth ion species including heavy rare earth elements have been demonstrated to migrate in solids, only a few light rare earth ion conductors have been developed so far due to their large ionic radius and in particular, cerium (Ce^{3+}) and praseodymium (Pr^{3+}) ions have not been

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considered to be suitable candidates for the conducting ion species in solid electrolytes because of the appearance of an electronic conduction due to their valence change in addition to their large ion size. However, since 2002, we have successfully developed a pure Ce^{3+} ion conductor, $(Ce_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ [11] and a pure Pr^{3+} ion conductor composite, $(Pr_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3 + NbPO_5$ [12] by strictly selecting the NASICON type phosphate containing three higher valent cations such as Zr^{4+}, Nb^{5+}, P^{5+} which tightly bond to the lattice constituent oxide anions in the solid compared with conducting trivalent cations. Furthermore, these solids exhibited considerably higher ion conductivity compared with the conductivity region of conventional trivalent ion conductors and the values were comparable to those for the representative divalent oxide anion conductors such as yttria stabilized zirconia (YSZ) [13] and calcia stabilized zirconia (CSZ) [13]. While Ce^{3+} ion or Pr^{3+} ion, which holds both trivalent and tetravalent state, have been demonstrated to conduct in $(R_xZr_{1-x})_{4/(4-x)}Nb(PO_4)_3$ series (R = Ce, Pr), other rare earth ion conductors have not been reported in the NASICON type $(R_xZr_{1-x})_{4/(4-x)}Nb(PO_4)_3$ series so far.

In the present study, among the rare earth ion species, especially, the light rare earth ion (La^{3+}, Nd^{3+}, Gd^{3+}) conductors in the $(R_xZr_{1-x})_{4/(4-x)}Nb(PO_4)_3$ (R: rare earths) series with the NASICON type structure were prepared and their ion conducting properties in solids were investigated.

2. Experimental

Samples of $(R_xZr_{1-x})_{4/(4-x)}Nb(PO_4)_3$ (R: La, Nd, Gd) were prepared from $La(NO_3)_3{\cdot}6H_2O$ (99.99%), Nd_2O_3 (99.9%), $Gd(NO_3)_3{\cdot}6H_2O$ (99.5%), ZrO_2 (99.99%), Nb_2O_5 (99.99%), and $(NH_4)_2HPO_4$ (99.99%). The compounds were mixed in an agent pot at a rotation speed of 300 rpm for 12 h by a ball milling method (Pulverisette 7, FRITSCH GmbH). The mixed powder was heated at 600 °C for 6 h, and then 1300 °C for 12 h in air. The samples obtained were characterized by X-ray powder diffraction (XRD) analysis using Cu Kα radiation (MultiFlex, Rigaku). The AC conductivities of samples were measured on the sintered pellets (sintered at 1300 °C for 12 h) coated with platinum-sputtered layer on both center surfaces by a complex impedance method over the frequency range 5 Hz to 13 MHz (Hewlett-Packard precision LCR meter, 4192A) in the temperature range of 300–600 °C in air. The polarization measurements were carried out in oxygen ($P_{O_2} = 10^5$ Pa) or in nitrogen ($P_{O_2} = 40$ Pa) atmosphere by applying a DC current of 1 μA through the sample pellet and the corresponding DC voltage over the sample with Pt mesh electrodes was measured as a function of time. DC electrolysis was carried out by applying a DC voltage of 3 V for 240 h at 800 °C with ion-blocking Pt bulk electrodes. After the electrolysis, the cathodic surface of the sample was analyzed by scanning electron microscope (SEM) (S-800, Hitachi) and electron probe microanalysis (EPMA) method (EPMA-1500, Shimadzu).

3. Results and discussion

From the XRD measurements, all the $(R_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ (R: La, Nd, Gd) solids prepared were found to possess the single phase of the NASICON type structure with a hexagonal symmetry. The lattice volume dependencies on the trivalent R^{3+} ionic radius, calculated from the XRD results for the present $(R_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ series, are presented in Fig. 1; the values for the $(R_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ (R: Ce, Pr) solids [11,12] are also shown. The lattice volume expands monotonically with the increase of the trivalent ionic radius except for $(Ce_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$. These results indicate that the $(R_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ (R: La, Nd, Gd) solid solution was successfully formed. Here, only the lattice volume of $(Ce_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ solid deviates from the above-mentioned proportional relation. This is probably due to the fact that 10% of the Ce ions in the sample exist in the tetravalent Ce^{4+} (0.101 nm; CN = 6) [14] state (viz. 90% of the Ce ions exit in the trivalent Ce^{3+} (0.115 nm; CN = 6) [14] state) and the smaller Ce^{4+} ion functions as the constituent of the framework to shrink the NASICON framework. Furthermore, $(Ce_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ is not chemically stable enough to utilize as a practical trivalent ion conductor because Ce^{4+} ion in the sample changes to Ce^{3+} in a reducing atmosphere, resulting in an appearance of n-type electronic conducting characteristics.

The electrical conductivity for the $(R_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ (R: La, Nd, Gd), measured at 600 °C, and the activation energy are plotted as a function of the trivalent ionic radius with the corresponding data of $(Pr_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ in Fig. 2. The conductivity depends on the ion size and it is evident that the most suitable ion size for the trivalent ion conduction exists in the present NASICON type phosphates series. From the figure, it becomes clear that the $(R_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ (R: Pr, Nd) solids exhibit almost the same values, which are the highest among the $(R_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ (R: La, Pr, Nd, Gd) series. However, the $(Pr_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ solid does not hold the single NASICON type phase but two phase composite

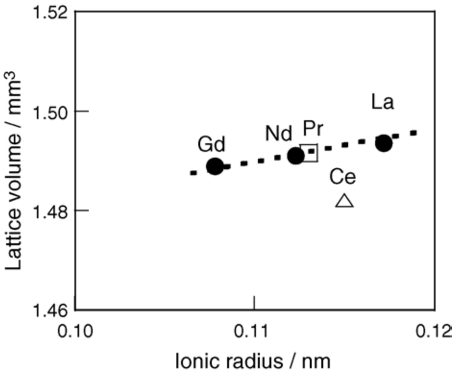

Fig. 1. The lattice volume dependencies on the trivalent R^{3+} ionic radius for $(R_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ (R = La, Nd, Gd) (●) with the data of $(Ce_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ (△) and $(Pr_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3 + NbPO_5$ (□).

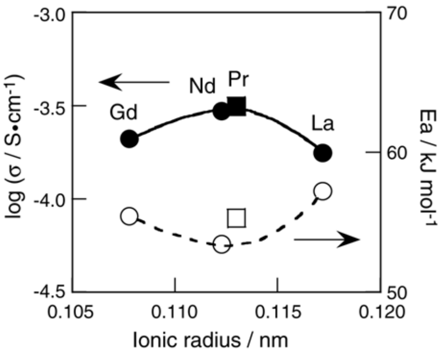

Fig. 2. The trivalent R^{3+} ionic radius dependencies of the electrical conductivity at 600 °C and the activation energy for $(R_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ (R = La, Nd, Gd) with the data of $(Pr_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3 + NbPO_5$.

of the NASICON phase and $NbPO_5$, resulting in a higher activation energy than its counterpart. Therefore, it is clear that the $(Nd_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ solid with the single NASICON phase is the most suitable conductor among the $(R_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ (R: La, Pr, Nd, Gd) series for practical use due to showing both the highest conductivity and the lowest activation energy.

The oxygen partial pressure dependencies of the AC conductivity for $(Nd_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ at 600 °C was measured. No conductivity change was observed by changing the oxygen partial pressure between 10^5 and 10^{-8} Pa and this phenomenon suggests that the predominant conducting species is only ion and neither electron nor hole.

Furthermore, the polarization measurements were performed by measuring the DC to AC conductivity (σ_{DC}/σ_{AC}) ratio as a function of time in both oxygen ($P_{O_2} = 10^5$ Pa) and nitrogen ($P_{O_2} = 40$ Pa) atmosphere. An abrupt decrease in the (σ_{DC}/σ_{AC}) ratio was recognized in both atmospheres and the ratios after 30 min were both below 0.01, indicating that the oxide anion conduction did not appear in the $(Nd_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ solid as demonstrated in Ref. [6]. Therefore, the migrating species in the solid is found to be limited to only the cation species.

In order to directly determine the conducting cation species, the DC electrolysis was performed by sandwiching the $(Nd_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ sintered pellet between two platinum bulk electrodes. Before the electrolysis, the decomposition voltage of the sample was identified to be ca. 1.9 V from the preliminary current–voltage measurement. The higher voltage than the decomposition voltage was applied in order to generate cation species at the anodic side in itself and force the migrating cations to conduct from anode to cathode direction continuously. Deposits were clearly observed on the cathodic surface of the electrolyzed sample after the electrolysis. The EPMA spot analyses were carried out on the representative deposit and the result is shown in Table 1. Among the elements in the sample, a remarkable increase was observed only for Nd element compared with that of the sample before the electrolysis. These results suggest that the predominant conducting species in the $(Nd_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ solid is clearly demonstrated to be Nd^{3+} cation.

Table 1
The EPMA spot analyses of the deposit on the cathodic surface of the $(Nd_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ before and after the electrolysis

Elements	Mother bulk before the electrolysis	Deposit on the cathodic surface after the electrolysis
Nd	2.3	17.7
Zr	21.5	20.6
Nb	19.6	12.1
P	56.6	49.6

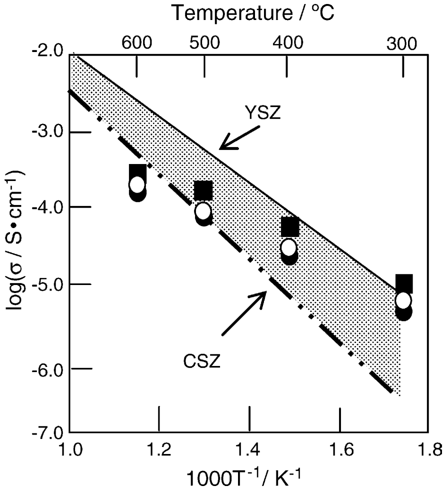

Fig. 3. The temperature dependencies of the trivalent ion conductivity for $(R_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ (R = La (●); R = Nd (■); R = Gd (○)) with the data of the representative divalent oxide anion conducting YSZ [13] and CSZ [13]. The typical O^{2-} ion conductivity region is also shown as the shaded area.

Fig. 3 presents the temperature dependencies of the trivalent ion conductivity for $(R_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ (R: La, Nd, Gd) and the region of those for the representative divalent oxide anion conducting YSZ [13] and CSZ [13] which have been already commercialized. The ion conductivities of the $(R_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ (R: La, Nd, Gd) solid electrolytes below 500 °C are located in the conductivity range of the representative divalent oxide anion conductors, and a trivalent ion conductivity higher than 10^{-4} S cm^{-1} at a temperature higher than 500 °C was obtained for R = La^{3+}, Nd^{3+}, Gd^{3+} in the $(R_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ series.

4. Conclusions

New trivalent rare earth cation conductors, $(R_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ (R: La, Nd, Gd), with the single phase of the NASICON type structure were successfully developed. It becomes clear that the suitable lattice volume for the R^{3+} ion conduction exists in the present trivalent phosphate series with the NASICON type structure from the relationship between the conducting trivalent ion size and the lattice volume. Since the $(R_{0.1}Zr_{0.9})_{40/39}Nb(PO_4)_3$ (R: La, Nd, Gd) solid electrolytes possess the high trivalent ion conductivity which is comparable to that of YSZ and CSZ, applications in functional devices such as chemical sensors are greatly expected.

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