Novel Multivalent Cation Conducting Ceramics and Their Application

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新規な多価カチオン伝導性セラミックスの開発とその応用

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Among the trivalent ion conductor series of $\text{Sc}_2(\text{WO}_4)_3$ type and NASICON type that we have reported, the highest ion conductivity was obtained for the trivalent Al^{3+} ion conducting NASICON type $(\text{Al}_x\text{Zr}_{1-x})_{4/(4-x)}\text{Nb}(\text{PO}_4)_3$ solid electrolyte and the value enters the area between yttria stabilized zirconia (YSZ) and calcia stabilized zirconia (CSZ) of well known commercialized high oxide anion conductors. The enhancement of both the ion conductivity and the mechanical strength was simultaneously realized by adding B_2O_3 as a sintering agent during the sintering procedure. The Al^{3+} ion conducting $(\text{Al}_x\text{Zr}_{1-x})_{4/(4-x)}\text{Nb}(\text{PO}_4)_3$ solid electrolyte with the B_2O_3 additive was combined with YSZ, and the refractory oxide based solid was set on the $(\text{Al}_x\text{Zr}_{1-x})_{4/(4-x)}\text{Nb}(\text{PO}_4)_3$ solid surface as the individual auxiliary electrode for carbon dioxide (CO_2), nitrogen oxides (NO_x), sulfur dioxide (SO_2) gas sensing, respectively. The sensor response was rapid, reproducible and continuous with obeying the Nernst theoretical relationship.

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1. Introduction

THERE are unique solids that the ion conduction only occurs without any hole or electron migration. Such peculiar solids are called “Solid Electrolytes or Ion Conducting Solids” and have been already practically applied for batteries and some chemical sensors.^(1,2) Among the ion species conducting in solids, monovalent and divalent ions (cations and anions) are popular migrating species in solids. In 1995,⁽³⁾ macroscopic trivalent cation conduction in solids was firstly demonstrated by us and after that, various kinds of trivalent cations such as Al^{3+} , In^{3+} , and rare earth cations, are clearly shown to conduct in solids in such structures as $\text{Sc}_2(\text{WO}_4)_3$ type^{(3)–(42)} and NASICON type.^{(43)–(53)} Among various trivalent cation species, Al^{3+} is one of the most practically applicable cation, and especially, $(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3$ with the NASICON type structure,⁽⁵⁰⁾ has been demonstrated to hold as high ion conductivity as yttria stabilized zirconia (YSZ)⁽⁵⁴⁾ and calcia stabilized zirconia (CSZ)⁽⁵⁴⁾ have.

While the $(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3$ solid shows a high ion conductivity, the higher ion conductivity is requested in addition to its mechanical strength. In order to improve both the mechanical strength and the density of the polycrystalline solid electrolyte simultaneously, one of most suitable ways is to enhance the sinterability by diminishing the pores appearing at the grain boundaries in the polycrystalline $(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3$ solid. One of attractive methods to enhance the sinterability is to add some additives with the sample powder. Recently, we have succeeded in enhancing the sinterability and as a result, the ion conductivity of the trivalent Sc^{3+} ion conducting $\text{Sc}_2(\text{WO}_4)_3$ polycrystalline solids was also improved by using the sintering additives of B_2O_3 ⁽⁵⁵⁾ or GeO_2 .⁽⁵⁶⁾ For the purpose of improving both the ion conducting characteristics and the mechanical strength of $(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3$, the low-melting oxide sintering additive of boron oxide (B_2O_3) (m.p. ca. 450°C) was mixed with the Al^{3+} ion conducting $(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3$ solid and heated for obtaining a high sintered solid.

In this article, the appreciably high Al^{3+} ion conducting $(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3$ solid having a suitable mechanical strength, was combined with YSZ with the auxiliary sensing electrode solid for CO_2 , NO_x , and SO_2 gas sensing, respectively, on the $(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3$ solid surface, and their gas sensing properties were summarized.

2. NASICON type trivalent ion conducting solid electrolytes 2.1 NASICON type trivalent ion (Al^{3+} , Ce^{3+} , Pr^{3+}) conductors

NASICON is one of well-known suitable structure for ion conduction and we have succeeded in developing the trivalent cation ($(\text{Al}^{3+},^{50}) \text{Ce}^{3+},^{51}) \text{Pr}^{3+},^{53})$) conductors with the NASICON type, showing as high temperature stability as 1300°C. The X-ray powder diffraction results for $(\text{M}_x\text{Zr}_{1-x})_{4/(4-x)}\text{Nb}(\text{PO}_4)_3$ ($\text{M} = \text{Al} (x=0.2, 0.3)$, $\text{Ce} (x=0.1, 0.2)$, and $\text{Pr} (x=0.05)$) are presented in Fig. 1. In the case that the trivalent Al^{3+} ion is the mobile species, the single NASICON type phase was obtained for the Al^{3+} ion up to $x=0.2$. Further Al^{3+} addition in the solid results in the formation of the additional NbPO_5 phase. In contrast, in the case for $\text{M} = \text{Ce}$ and Pr in $(\text{M}_x\text{Zr}_{1-x})_{4/(4-x)}\text{Nb}(\text{PO}_4)_3$, the secondary NbPO_5 phase additionally appears with the NASICON type phase at $x=0.2$ and 0.05, respectively. The smaller Al^{3+} ion compared with Ce^{3+} and Pr^{3+} is more likely to be included in the NASICON type phase.

Figure 2 shows the ionic conductivity change with x in $(\text{M}_x\text{Zr}_{1-x})_{4/(4-x)}\text{Nb}(\text{PO}_4)_3$ ($\text{M} = \text{Al}$, Ce , and Pr). In the case for the $(\text{Al}_x\text{Zr}_{1-x})_{4/(4-x)}\text{Nb}(\text{PO}_4)_3$ solid electrolyte, the conductivity becomes maximum at $x=0.2$. In contrast, the highest ion conductivity is obtained at $x=0.1$ in $(\text{M}_x\text{Zr}_{1-x})_{4/(4-x)}\text{Nb}(\text{PO}_4)_3$ ($\text{M} = \text{Ce}$ and Pr).

The temperature dependencies of the trivalent ion conductivity for Al^{3+} , Ce^{3+} , and Pr^{3+} are depicted in Fig. 3, respectively. Activation energies calculated from the $\log(\sigma T)$ vs. $1/T$ relationship for $\text{M} = \text{Al}$, Ce , and Pr in the $(\text{M}_x\text{Zr}_{1-x})_{4/(4-x)}\text{Nb}(\text{PO}_4)_3$ solid electrolytes, are 52.4, 54.1, and 55.3 kJ·

Fig. 1. X-ray powder diffraction results for $(M_xZr_{1-x})_{4/(4-x)}Nb(PO_4)_3$ ($M=Al(x=0.2, 0.3)$, $Ce(x=0.1, 0.2)$, and $Pr(x=0.05)$) and $NaZr_2(PO_4)_3$.

Fig. 2. Ionic conductivity change with x in $(M_xZr_{1-x})_{4/(4-x)}Nb(PO_4)_3$ ($M=Al, Ce$, and Pr).

mol^{-1} , respectively. The ion conductivities of all three types of $(M_xZr_{1-x})_{4/(4-x)}Nb(PO_4)_3$ solids enter into the ion conductivity region between yttria stabilized zirconia (YSZ) and calia stabilized zirconia (CSZ).

Among three types of cation conducting solids, the highest ion conductivity ($4.4 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ at 600°C) and the lowest activation energy (E_a) for ion conduction are obtained for the Al^{3+} ion conducting solid.

2.2 B₂O₃ addition

Figure 4 shows the X-ray powder diffraction results of the $(Al_{0.2}Zr_{0.8})_{20/19}Nb(PO_4)_3$ solids with various B_2O_3 addition and that of pure $(Al_{0.2}Zr_{0.8})_{20/19}Nb(PO_4)_3$. The samples with the B_2O_3 additive lower than 6 wt%, were found to possess the single phase of the NASICON type structure with hexagonal symmetry. From the ICP measurements, the boron content was found to be less than the detection limit of 10 ppb for all the samples sintered and the B_2O_3 additive was found to have vaporized during the sintering procedure. In contrast, for the samples with more than 6 wt% B_2O_3 , the phases formed are the three phase mixture of the NASICON type $(Al_{0.2}Zr_{0.8})_{20/19}Nb(PO_4)_3$, ZrP_2O_7 , and $P_2O_5 \cdot 9Nb_2O_5$, suggesting the decomposition of the NASICON type phase. From the results described above, it is evident that the opti-

Fig. 3. Temperature dependencies of the trivalent ion conductivity for Al^{3+} , Ce^{3+} , and Pr^{3+} , respectively. The corresponding data for YSZ and CSZ is shown as dotted and solid lines, respectively.

Fig. 4. X-ray powder diffraction results of the $(Al_{0.2}Zr_{0.8})_{20/19}Nb(PO_4)_3$ solids with various B_2O_3 addition and that of pure $(Al_{0.2}Zr_{0.8})_{20/19}Nb(PO_4)_3$.

mum amount of the B_2O_3 additive to form the single NASICON type phase is ca. 6 wt%.

From the polarization measurements for the $(Al_{0.2}Zr_{0.8})_{20/19}Nb(PO_4)_3$ sample with the 6 wt% B_2O_3 addition in oxygen ($PO_2: 10^5 \text{ Pa}$) and in nitrogen ($PO_2: 40 \text{ Pa}$) atmospheres at 600°C , it becomes clear that the dc to ac conductivity ratio (σ_{dc}/σ_{ac}) abruptly reduces in both atmospheres with time and reduces lower than 0.005 after 30 min, which is a similar phenomenon observed in the case for the pure Al^{3+} ion conducting $(Al_{0.2}Zr_{0.8})_{20/19}Nb(PO_4)_3$ solid.⁵⁰⁾ The results described above clearly deny the probability of oxide anion, hole, or electron conduction and the cation transference number is estimated to be higher than 0.995 from the (σ_{dc}/σ_{ac}) ratio. Furthermore, dc electrolysis was conducted for the purpose of directly identifying the conducting cation species in the phosphate solid with the 6 wt% B_2O_3 additive. After dc electrolysis, the deposits were clearly observed on the cathodic surface and from the EPMA measurement, the content of the

Fig. 5. Temperature dependencies of the ion conductivity for $(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3$ with the addition of 6 wt% B_2O_3 (closed circle) in addition to the sample without B_2O_3 addition (open square) previously reported.⁵⁰⁾ The corresponding data for ZrP_2O_7 (dotted) and $\text{P}_2\text{O}_5 \cdot 9\text{Nb}_2\text{O}_5$ (solid) are also plotted.

Al element in the deposits enhances around twenty times compared with that of the sample before the electrolysis, similar to the dc electrolysis result for the pure Al^{3+} ion conducting $(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3$ solid electrolyte.⁵⁰⁾ From the results described above, the present $(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3$ solid prepared by the addition of 6 wt% B_2O_3 was concluded to be a pure Al^{3+} ion conducting solid electrolyte.

Figure 5 shows the temperature dependencies of the ion conductivity for $(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3$ with the addition of 6 wt% B_2O_3 (closed circle) in addition to the sample without B_2O_3 addition (open square). The Al^{3+} ion conductivity (at 600°C) of the $(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3$ solid with B_2O_3 is twice as high as that of the sample without B_2O_3 . In addition, Vickers hardness of the sintered sample increases from 189 to 367 by the B_2O_3 addition. The conductivity improvement is mainly attributed to the reduction of pores appeared in the pellets by sintering with B_2O_3 and results in the enhancement of the sinterability.

3. Application

3.1 Carbon dioxide gas sensor

Since the suitable solid electrolyte of $(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3$, having both a satisfactory Al^{3+} ion conductivity and a high mechanical strength, was realized, the Al^{3+} ion conducting $(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3$ solid prepared by the 6 wt% B_2O_3 addition, was selected as the optimum candidate for one of the gas sensor element among the trivalent ion conductors of $\text{Sc}_2(\text{WO}_4)_3$ type and NASICON type series. The Al^{3+} ion conducting $(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3$ solid electrolyte was combined with YSZ and a new type of practical CO_2 gas sensor operating at the temperature of 500°C, was fabricated as illustrated in Fig. 6. Here, the water-insoluble oxysulfate based solid of $0.8\text{La}_2\text{O}_3\text{SO}_4 \cdot 0.2\text{Li}_2\text{CO}_3$ was prepared and applied as the auxiliary CO_2 sensing electrode. The detail is described in Refs. 57)–60).

The inserted figure in Fig. 7 depicts one of typical sensor

Fig. 6. A new type of practical CO_2 gas sensor operating at the temperature of 500°C.

Fig. 7. Relationship between the sensor EMF output and the logarithm of the CO_2 concentration. The inserted figure depicts one of typical sensor response curves observed when the CO_2 gas concentration was varied from 500 ppm to 1%.

response curves observed when the CO_2 gas concentration was varied from 500 ppm to 1%. The response time to obtain a 90% total response was within a min and the continuous response was clearly obtained. The relationship between the sensor EMF output observed in the inserted figure and the logarithm of the CO_2 concentration is plotted in Fig. 7 as the closed circles. The theoretical slope ($n=2.00$) calculated from the two electron chemical reaction of the Nernstian relationship (Details see Ref. 59) is also shown as a solid line in Fig. 7. With the increase of the CO_2 gas concentration, the sensor output monotonously decreases and a linear 1 : 1 relationship was clearly recognized between the sensor output and the logarithm of the CO_2 gas concentration and the slope obtained from closed circles is $n=1.92$. The n value is in a satisfactory accordance with the calculated value of $n=2.00$, indicating a theoretical Nernst response. The proto-type carbon dioxide sensor was fabricated as presented in Fig. 8 and the same sensing performance has been already demonstrated.

3.2 Nitrogen oxides (NO_x) gas sensor

The key factor for gas sensing is the sensing auxiliary electrode and the another gas sensing would be realized by replacing the auxiliary sensing electrode. Here, the oxysulfate based electrode of $0.8\text{La}_2\text{O}_3\text{SO}_4 \cdot 0.2\text{Li}_2\text{CO}_3$ was replaced by the nitrate doped rare earth oxide based electrode.^{61)–65)} One of

Fig. 8. Proto-type carbon dioxide sensor.

Fig. 9. Relationship between the sensor EMF output and the logarithm of the NO concentration. The inserted figure depicts one of typical sensor response curves observed when the NO gas concentration was varied from 2000 to 200 ppm and vice versa. (Reproduced with permission from Ref. 64). Copyright 2004 The Electrochemical Society Inc.)

representative sensor response curves observed when the NO gas content was varied is shown in the inserted figure in **Fig. 9**, with varying the gas concentration from 2000 to 200 ppm and vice versa of the typical NO gas content region in an emitted gas atmosphere. The response time defined as the time to obtain a 90% total response was within ten min and a continuous, and reproducible response was observed.

The sensor EMF outputs observed in the inserted figure in **Fig. 9** for in increasing and in decreasing the NO gas concentration are plotted in **Fig. 9** as closed squares and open circles, respectively. The sensor output monotonously reduced with increasing the NO gas content and a 1 : 1 linear relationship was obtained in the relation between the sensor output and the logarithm of the NO gas content. The slope ($n=1.00$) obtained from the theoretical Nernst relation is also presented as a solid line in **Fig. 9**. The n values from the slope for increasing and decreasing the NO gas content, are 1.03 and 1.01, respectively. Those values almost coincide with the calculated value of $n=1.00$, demonstrating a theoretical Nernst response.

The present sensor cell was examined for sensing NO_2 of

Fig. 10. Relationship between the sensor EMF output and the logarithm of the NO_2 concentration. The inserted figure depicts one of typical sensor response curves observed when the NO_2 gas concentration was varied from 2000 to 200 ppm and vice versa. (Reproduced with permission from Ref. 64). Copyright 2004 The Electrochemical Society Inc.)

Fig. 11. Relationship between the sensor output and the logarithm of the NO (in decreasing) or NO_2 (in increasing) gas content at 450°C. (Reproduced with permission from Ref. 64). Copyright 2004 The Electrochemical Society Inc.)

another representative nitrogen oxides gas that also exists in an emitted gas atmosphere. The sensor EMF output vs. the logarithm of the NO_2 gas content is shown in **Fig. 10** and one of typical response curve observed by the NO_2 gas variation is shown in the insert figure in **Fig. 10**. The sensor output values for both increasing and decreasing the gas concentration is similar and the slope obtained from increasing (closed squares) the NO_2 gas and in decreasing (open circles) the gas are $n=1.01$ and 1.00, respectively. By comparing the sensor EMF outputs between **Figs. 9** and **10**, the present sensor is greatly expected to operate as the in-situ total NO_x (NO plus NO_2) gas sensing tool. The relationship between the sensor output and the logarithm of the NO (in decreasing (open circle)) or NO_2 (in increasing (closed square)) gas content at 450°C is summarized in **Fig. 11**. The sensor EMF output is almost identical, indicating that the total (NO plus NO_2) gas

Fig. 12. Sensor output deviation with the variation of the NO and NO₂ gas content ratio (fixing the total NO_x gas concentration at 2000 ppm). (Reproduced with permission from Ref. 64). Copyright 2004 The Electrochemical Society Inc.)

Fig. 13. Relationship between the sensor EMF output and the logarithm of the SO₂ concentration at 500°C. The inserted figure depicts one of typical sensor response curves observed when the SO₂ gas concentration was varied from 200 to 2000 ppm and vice versa. (Reproduced with permission from Ref. 67). Copyright 2005 American Scientific Publishers.)

concentration can be monitored by the present sensor.

The sensor output deviation with the variation of the NO and NO₂ gas content ratio (fixing the total NO_x gas concentration at 2000 ppm) is presented in **Fig. 12**. By changing the NO vs. NO₂ gas ratio from 9 : 1 to 1 : 9, any meaningful deviation in the sensor output was not observed at all, indicating that the present sensor can detect the total NO_x gas concentration, irrespective of the NO vs. NO₂ ratio in total NO_x gases.

3.3 Sulfur dioxide gas sensor

Another toxic gas deteriorating the environment is sulfur dioxide.^{66),67)} Here, oxysulfate based refractory solid (0.7 La₂O₃SO₄·0.3Li₂SO₄) was applied as the SO₂ gas sensing auxiliary electrode.

The inserted figure in **Fig. 13** shows a representative sensor response curve observed when the SO₂ gas concentration was varied from 200 to 2000 ppm and vice versa at 500°C. The sensor EMF outputs at the same SO₂ gas content were almost identical in both increasing (open squares) and in decreasing

(closed circles) the concentration, and the response time, defined as the time to reach a 90% total response, was within two min, demonstrating a rapid and reversible response for the SO₂ gas sensing.

The sensor outputs observed in the inserted figure in **Fig. 13** are plotted in **Fig. 13** and the Nernst theoretical slope ($n=2.00$) calculated from the Nernst equation is also drawn as a solid line in **Fig. 13**. The sensor outputs increase monotonically with the increase of the SO₂ gas content and a 1 : 1 linear relationship was clearly observed between the sensor output and the logarithm of the SO₂ gas content. In addition, the n values obtained from the slope for increasing and decreasing the SO₂ gas content in **Fig. 13** are 1.98 and 1.90, respectively. These values are consistent with the theoretical value calculated from the Nernst equation.

4. Conclusions

New types of trivalent cation conducting solids were successfully realized by selecting the NASICON type structure for ion conduction. Among the trivalent cation species, aluminum cation was selected as the most appropriate cation and the NASICON type solid of (Al_{0.2}Zr_{0.8})_{20/19}Nb(PO₄)₃ was successfully obtained. For the purpose of enhancing the Al³⁺ ion conducting characteristics, boron oxide was added as the sintering additive and it is demonstrated that the B₂O₃ addition in the Al³⁺ ion conducting (Al_{0.2}Zr_{0.8})_{20/19}Nb(PO₄)₃ solid was considerably effective to enhance the mechanical strength as well as the Al³⁺ ion conductivity. The (Al_{0.2}Zr_{0.8})_{20/19}Nb(PO₄)₃ solid electrolyte with the B₂O₃ addition was combined with divalent oxide anion conducting stabilized zirconia (YSZ) and the corresponding gas sensing electrode was attached on the (Al_{0.2}Zr_{0.8})_{20/19}Nb(PO₄)₃ solid surface as the auxiliary gas sensing electrode. The sensor EMF output was continuous, rapid and reproducible with obeying the theoretical Nernst relationship, demonstrating a practical applicable gas sensing performance.

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