Novel Multivalent Cation Conducting Ceramics and Their Application

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Amongs 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 $\text{Al}^{3+}$ ion conducting NASICON type ($\text{Al}_{x}\text{Zr}_{1-x}$$\text{O}_{4}/\text{Ga}$) $\text{Nb}$($\text{PO}_4$)$_3$ solid electrolyte and the value enters the area between yttria stabilized zirconia (YSZ) and calcium stabilized zirconia (CSZ) of well known commercial high oxide anion conductors. The enhancement of both the ion conductivity and the mechanical strength was simultaneously realized by adding $\text{B}_2\text{O}_3$ as a sintering agent during the sintering procedure. The $\text{Al}^{3+}$ ion conducting ($\text{Al}_{x}\text{Zr}_{1-x}$$\text{O}_{4}/\text{Ga}$)$\text{Nb}$($\text{PO}_4$)$_3$ solid electrolyte with the $\text{B}_2\text{O}_3$ additive was combined with YSZ, and the refractory oxide based solid was set on the ($\text{Al}_{x}\text{Zr}_{1-x}$$\text{O}_{4}/\text{Ga}$)$\text{Nb}$($\text{PO}_4$)$_3$ solid surface as the individual auxiliary electrode for carbon dioxide ($\text{CO}_2$), nitrogen oxides ($\text{NO}_x$), sulfur dioxide ($\text{SO}_2$) gas sensing, respectively. The sensor response was rapid, reproducible and continuous with obeying the Nernst theoretical relationship.

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

2.2 B\(_2\)O\(_3\) Addition

Figure 4 shows the X-ray powder diffraction results of the \((\text{Al}_{3}2,2\text{Zr}_{0.8},19\text{Nb}(\text{PO}_4)_3)\) solids with various B\(_2\)O\(_3\) addition and that of pure \((\text{Al}_{3}2,2\text{Zr}_{0.8},19\text{Nb}(\text{PO}_4)_3)\). The samples with the B\(_2\)O\(_3\) 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 0.1 ppm for all the samples sintered and the B\(_2\)O\(_3\) additive was found to have vaporized during the sintering procedure. In contrast, for the samples with more than 6 wt\% B\(_2\)O\(_3\), the phases formed are the two phase mixture of the NASICON type \((\text{Al}_{3}2,2\text{Zr}_{0.8},19\text{Nb}(\text{PO}_4)_3), \text{ZrP}_2\text{O}_7, \text{and P}_2\text{O}_5\cdot9\text{Nb}_2\text{O}_5, \) suggesting the decomposition of the NASICON type phase. From the results described above, it is evident that the optimum amount of the B\(_2\)O\(_3\) additive to form the single NASICON type phase is ca. 6 wt\%.

From the polarization measurements for the \((\text{Al}_{3}2,2\text{Zr}_{0.8},19\text{Nb}(\text{PO}_4)_3)\) sample with the 6 wt\% B\(_2\)O\(_3\) addition in oxygen \((\text{PO}_2; 10^5 \text{ Pa})\) and in nitrogen \((\text{PO}_2; 40 \text{ Pa})\) atmospheres at 600°C, it becomes clear that the dc to ac conductivity ratio \( \sigma_{dc}/\sigma_{ac} \) 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 \( \text{Al}^{3+} \) ion conducting \((\text{Al}_{3}2,2\text{Zr}_{0.8},19\text{Nb}(\text{PO}_4)_3)\) solid.\(^{30}\) The results described above clearly deny the probability of oxide ion, hole, or electron conduction and the cation transference number is estimated to be higher than 0.995 from the \( \sigma_{dc}/\sigma_{ac} \) 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\(_2\)O\(_3\) additive. After dc electrolysis, the deposits were clearly observed on the cathodic surface and from the EPMA measurement, the content of the
The present/\text{Ga}\text{ducting} enhancement of the sinterability.

Sensor operating at the temperature of 500/\text{Ga}\text{conducting} activity prepared by the addition of 6 wt \% \text{B}_2\text{O}_3 (closed circle) in addition to the sample without \text{B}_2\text{O}_3 addition (open square) previously reported.\text{Ga}\text{ducting} The corresponding data for \text{ZrP}_2\text{O}_7 (dotted) and \text{P}_2\text{O}_5\text{·9B}_2\text{O}_3 (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}_2\text{Zr}_{0.8}\text{Nb}_{0.2}\text{PO}_4)_3 solid electrolyte.\text{Ga}\text{ducting} From the results described above, the present (\text{Al}_2\text{Zr}_{0.8}\text{Nb}_{0.2}\text{PO}_4)_3 solid prepared by the addition of 6 wt \% \text{B}_2\text{O}_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}_2\text{Zr}_{0.8}\text{Nb}_{0.2}\text{PO}_4)_3 with the addition of 6 wt \% \text{B}_2\text{O}_3 (closed circle) in addition to the sample without \text{B}_2\text{O}_3 addition (open square). The Al$^{3+}$ ion conductivity (at 600°C) of the (\text{Al}_2\text{Zr}_{0.8}\text{Nb}_{0.2}\text{PO}_4)_3 solid with \text{B}_2\text{O}_3 is twice as high as that of the sample without \text{B}_2\text{O}_3. In addition, Vickers hardness of the sintered sample increases from 189 to 367 by the \text{B}_2\text{O}_3 addition. The conductivity improvement is mainly attributed to the reduction of pores appeared in the pellets by sintering with \text{B}_2\text{O}_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}_2\text{Zr}_{0.8}\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}_2\text{Zr}_{0.8}\text{Nb}_{0.2}\text{PO}_4)_3 solid prepared by the 6 wt \% \text{B}_2\text{O}_3 addition was selected as the optimum candidate for one of the gas sensor element among the trivalent ion conductors of Sc$^2$(WO$_4$)$_3$ type and NASICON type series. The Al$^{3+}$ ion conducting (\text{Al}_2\text{Zr}_{0.8}\text{Nb}_{0.2}\text{PO}_4)_3 solid electrolyte was combined with YSZ and a new type of practical \text{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}_4·0.2\text{Li}_2\text{CO}_3 was prepared and applied as the auxiliary \text{CO}_2 sensing electrode. The detail is described in Refs. 57 – 60.

The inserted figure in Fig. 7 depicts one of typical sensor response curves observed when the \text{CO}_2 gas concentration was varied from 500 ppm to 1\%.

Fig. 6. A new type of practical \text{CO}_2 gas sensor operating at the temperature of 500°C.

Fig. 7. Relationship between the sensor EMF output and the logarithm of the \text{CO}_2 concentration. The inserted figure depicts one of typical sensor response curves observed when the \text{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 \text{CO}_2 concentration is plotted in Fig. 7 as the closed circles. The theoretical slope (n = 2.00) calculated from the tree 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 \text{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 \text{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 (\text{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}_4·0.2\text{Li}_2\text{CO}_3 was replaced by the nitrate doped rare earth oxide based electrode.\text{Ga}\text{ducting} One of...
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. 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 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 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 (in decreasing) or NO\(_2\) (in increasing) 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. 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.)

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.)
tion, irrespective of the NO vs. NO \(_2\) sor EMF outputs at the same SO \(_2\) varied from 200 to 2000 ppm and vice versa at 500 ppm.

**Fig. 12.** Sensor output deviation with the variation of the NO and NO \(_2\) gas content ratio (fixing the total NO \(_3\) gas concentration at 2000 ppm). (Reproduced with permission from Ref. 64. Copyright 2004 The Electrochemical Society Inc.)

The sensor output deviation with the variation of the NO and NO \(_2\) gas content ratio (fixing the total NO \(_3\) gas concentration at 200 ppm) is presented in **Fig. 12**. By changing the NO vs. NO \(_2\) 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 \(_3\) gas concentration, irrespective of the NO vs. NO \(_2\) ratio in total NO \(_3\) 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 La\(_2\)O\(_3\)-0.3Li\(_2\)SO\(_4\)) was applied as the SO \(_2\) gas sensing auxiliary electrode.

The inserted figure in **Fig. 13** shows a representative sensor response curve observed when the SO \(_2\) gas concentration was varied from 200 to 2000 ppm and vice versa at 500 ppm. The sensor EMF outputs at the same SO \(_2\) 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 SO \(_2\) 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 SO \(_2\) gas content and a 1 : 1 linear relationship was clearly observed between the sensor output and the logarithm of the SO \(_2\) gas content. In addition, the \(n\) values obtained from the slope for increasing and decreasing the SO \(_2\) 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 \((\text{Al}_2\text{Zr}_{0.5}\text{O}_3)_{20/19}\) \((\text{PO}_4)\), was successfully obtained. For the purpose of enhancing the \(\text{Al}^{3+}\) ion conducting characteristics, boron oxide was added as the sintering additive and it is demonstrated that the \(\text{B}_2\text{O}_3\) addition in the \(\text{Al}^{3+}\) ion conducting \((\text{Al}_2\text{Zr}_{0.5}\text{O}_3)_{20/19}\) \((\text{PO}_4)\) solid was considerably effective to enhance the mechanical strength as well as the \(\text{Al}^{3+}\) ion conductivity. The \((\text{Al}_2\text{Zr}_{0.5}\text{O}_3)_{20/19}\) \((\text{PO}_4)\) solid electrolyte with the \(\text{B}_2\text{O}_3\) addition was combined with divalent oxide anion conducting stabilized zirconia \((\text{YSZ})\) and the corresponding gas sensing electrode was attached on the \((\text{Al}_2\text{Zr}_{0.5}\text{O}_3)_{20/19}\) \((\text{PO}_4)\) 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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### References

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