

## CO<sub>2</sub> Gas Sensing with the Combination of Trivalent Al<sup>3+</sup> Ion Conducting Al<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub> Single Crystal Solid and Oxide Ion Conducting Stabilized Zirconia

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A carbon dioxide gas sensor was fabricated by using a trivalent Al<sup>3+</sup> ion conducting Al<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub> single crystal solid with an oxide ion conducting stabilized zirconia and Li<sub>2</sub>CO<sub>3</sub> as an auxiliary electrode. The sensor response was rapid and reproducible enough for a practical application. In addition, the sensor output was stable and the present sensor would be one of superior promising tool with a compact and maintenance-free type CO<sub>2</sub> gas sensing.

Carbon dioxide is a main gas species causing a global warming of the earth and the suppression of CO<sub>2</sub> emission into the atmosphere has been becoming an urgent issue to solve in a world wide scale. From the selective CO<sub>2</sub> detection principle, one of suitable mediums is sensing with solid electrolyte. As the mobile ion species for solid electrolytes, monovalent cations such as alkali metals,<sup>1-5</sup> and divalent cations like alkali earths,<sup>6,7</sup> and divalent oxide anion,<sup>8</sup> and recently trivalent ion such as Sc<sup>3+</sup> in Sc<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub><sup>9</sup> have been reported to work as the component of CO<sub>2</sub> sensor. Among those CO<sub>2</sub> detection assemblies, the combination of a cation conductor with an oxide anion conductor<sup>4,5,9</sup> has a great merit in avoiding the interference from the ambient atmosphere, since the oxide layer formed between two solid electrolytes is covered by both solid electrolytes to maintain the oxide surface as it formed.

The combination mentioned above is also greatly effective because that the oxide of migrating ion species exists in the interface between two solid electrolytes and the activity of the oxide determines the EMF output. However, in the case that monovalent ions such as alkali metals were applied, the alkali metal oxides are reactive and appreciably unstable to form other stable compounds to greatly deteriorate the sensing characteristics.

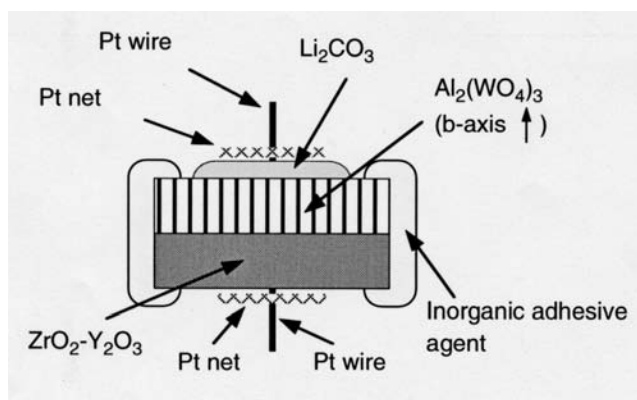
From the consideration of the oxide stability, we have demonstrated MgO<sup>10</sup> and Sc<sub>2</sub>O<sub>3</sub><sup>9</sup> are one of suitable oxides. However, the cation conductors applied are, in both cases, polycrystalline pellet and it possesses the grain boundaries which function as the degradation sites. In addition, the main cation species in Sc<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub> is considerably expensive Sc element in spite that the sensor should be installed at every emitting site. Therefore, in order to realize a global suppression of the CO<sub>2</sub> exhaustion effectively, it is essential to reduce the installation cost as much as possible, because the number of the sensor installation is huge.

In this letter, among the same trivalent ion conducting material series with Sc<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub> type, Al<sup>3+</sup> is selected as the migrating ion species, which exists very common on earth. Since the sensor element is exposed to various kinds of atmospheres, eg. high humidity, reducing or oxidizing atmospheres, the solid electrolyte should be as much stable as possible. From such a point of view, a single crystal form in which no

grain boundary exists, is adopted as the most appropriate candidate among the trivalent ion conducting Sc<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub> type series. In our previous paper,<sup>11</sup> we have succeeded in growing a trivalent Al<sup>3+</sup> ion conducting single crystal solid electrolyte and we have already clarified that the most preferential direction for trivalent Al<sup>3+</sup> ion conduction is to b-axis.<sup>12</sup>

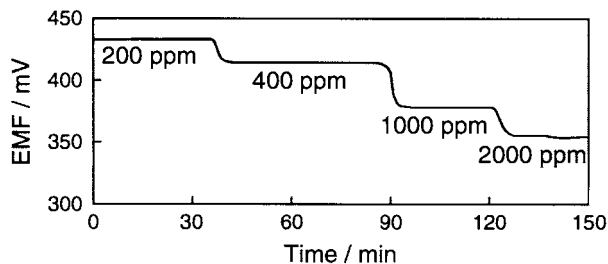
Here, the trivalent Al<sup>3+</sup> ion conducting single crystal was applied so as to make Al<sup>3+</sup> ion migrate toward the preferential b-axis direction with the combination of oxide anion conducting stabilized zirconia as the counter solid electrolyte and Li<sub>2</sub>CO<sub>3</sub> as an auxiliary electrode, and its CO<sub>2</sub> gas sensing performance was investigated.

An Al<sup>3+</sup> ion conducting single crystal was grown as described in our previous paper.<sup>11</sup> Oxide ion conducting stabilized zirconia was prepared by mixing ZrO<sub>2</sub>(purity: 99.9%) and Y<sub>2</sub>O<sub>3</sub>(purity: 99.9%) in a molar ratio of 9:1 and heated twice at 1600 °C for 12 h in air. The single crystal was set as shown in Figure 1 so that the Al<sup>3+</sup> ion conducting direction is parallel to the b-axis in the single crystal. Lithium metoxide(purity: 99.9%) pellet was fixed on the single crystal surface and heated up to the operating temperature of 550 °C for approximately 1 h in a 5% CO<sub>2</sub> gas diluted with air to form lithium carbonate layer. The CO<sub>2</sub> gas concentration of 1% and 200-2000 ppm was controlled by mixing CO<sub>2</sub>-air or 1% CO<sub>2</sub> diluted with nitrogen-air mixture, respectively. The total flowing rate was maintained constant at 100 ml/min. The sensor output was monitored by an electrometer(Advantest R8240).

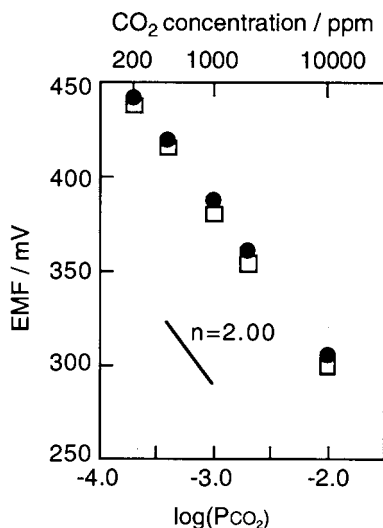


**Figure 1.** The cross-sectional view of the CO<sub>2</sub> sensor cell with the combination of trivalent Al<sup>3+</sup> ion conducting single crystal solid and O<sup>2-</sup> ion conducting stabilized zirconia with Li<sub>2</sub>CO<sub>3</sub> as an auxiliary electrode.

Figure 2 shows one of typical sensor output response curves with changing the CO<sub>2</sub> gas content. The response was rapid and continuous, indicating suitable characteristics for practical applications.



**Figure 2.** One of typical sensor output response curves with changing the CO<sub>2</sub> gas content.



**Figure 3.** The sensor output vs. logarithm of CO<sub>2</sub> concentration.

The reactions occur at the detecting electrode, interface between the detecting electrode and Al<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub> single crystal electrolyte, interface between two solid electrolytes, and the reference electrode and the derivation of the Nernst equation are similar as described in our previous letter.<sup>9</sup>

The Nernst equation is finally simplified as follows.

$$E = C_2(\text{constant}) - (R/nF)T \ln(\text{PCO}_2^{1/n}) \quad (n=2.00) \quad (1)$$

The sensor output vs. logarithm of CO<sub>2</sub> pressure is presented in Figure 3. In the CO<sub>2</sub> gas concentration from 200 ppm to 1%, a linear 1 to 1 relation is clearly observed. This result definitely indicates that the present CO<sub>2</sub> sensor can detect the CO<sub>2</sub> gas content accurately. The *n* value observed from the plot data (●) in Figure 3 is 2.03 and the value very well coincides with the theoretical value of *n*=2.00 (eq. (1)). The EMF output value (□) after several days is consistent with the output response described above (●). This result clearly means that the combination of Al<sup>3+</sup> ion conducting single crystal and an oxide anion conductor contributes greatly to stabilizing the

sensor output response.

In the case that the polycrystalline Al<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub> solid electrolyte is applied, the slope of the relation in EMF-log(PCO<sub>2</sub>) is 2.01. However, the output value deviates approximately 50 mV after several days, indicating that Li<sub>2</sub>CO<sub>3</sub> which has been used as the auxiliary electrode, diffuses into Al<sub>2</sub>(WO<sub>4</sub>)<sub>3</sub> polycrystal by permeating through grain boundaries. This happens since grain boundaries exist in the trivalent ion conductor and the behaviors demonstrate the suitability of applying single crystal where any grain boundaries do not exist.

The CO<sub>2</sub> sensor fabricated with the combination of trivalent Al<sup>3+</sup> ion conducting single crystal solid and O<sup>2-</sup> ion conducting stabilized zirconia with Li<sub>2</sub>CO<sub>3</sub> as an auxiliary electrode can detect the CO<sub>2</sub> gas, rapidly, accurately and reproducible response was also stably observed. The present sensor can be produced in a compact, inexpensive and maintenance-free type cell and is greatly expected to be applied in a commercial use in the near future.

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