Highly Water Durable NH_3 Gas Sensor Based on Al^{3+} Ion Conducting Solid Electrolyte with NH_4^+ -Gallate

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An ammonia gas sensor was fabricated using Al^{3+} ion conducting $(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3$ solid electrolyte with NH_4^+ - β -gallate (NH_4^+ - $\text{Ga}_{11}\text{O}_{17}$) as the auxiliary sensing electrode and its performance in humid atmosphere was investigated. The sensor exhibited advanced sensing performance than previously reported NH_3 gas sensors with a continuous, quantitative and reproducible response that obeys the theoretical Nernst relationship even in a highly humidified atmosphere containing 4.2 vol % H_2O at 230 °C. Therefore, the proposed sensor with NH_4^+ - β -gallate auxiliary sensing electrode is expected to be a suitable candidate for application as a practical *on-site* NH_3 gas detecting tool.

Key Words : Solid Electrolyte, Ammonia Gas Sensor, Aluminum Ion, Gallate

1 Introduction

Ammonia (NH_3) gas is extensively applied in industry; however, its high toxicity means that leakage of high-concentration ammonia gas would cause a serious disaster. Therefore, for the prevention of such accidents, accurate ammonia gas detection is required to raise alarm and identify the leakage site. Today, ammonia gas concentration is measured using analytical apparatus based on ion or gas chromatography. However, these are not suitable for *on-site* NH_3 gas sensing, because they require pretreatment of the sample gas. Furthermore, such equipment is too expensive and large to install at every NH_3 emission site. Therefore, development of a smart ammonia gas sensor is required to realize *on-site* monitoring at various emission sites. However, the interference of water vapor is a critical problem for accurate NH_3 sensing because NH_3 is usually present together with H_2O .

Although various types of compact NH_3 sensors have been proposed to date, a practical NH_3 sensor with highly selective and quantitative detection has not yet been developed. Solid electrolyte type sensors¹⁻⁴⁾ have significant advantages in sensitivity and selectivity based on the unique characteristics of solid electrolytes in that single ionic species can migrate in solids.

In our previous work on solid electrolyte type gas sensors,⁵⁻⁷⁾ we have demonstrated the superiority of the trivalent Al^{3+} ion conducting $(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3$ solid electrolyte⁸⁾ as a key sensor component material, and we have successfully developed CO_2 ,⁵⁾ NO_x ,⁶⁾ and SO_2 ⁷⁾ gas sensors that exhibit excellent sensing performance, such as high selectivity and long-term stability by selection of an appropriate auxiliary sensing electrode.

Therefore, fabrication of a NH_3 gas sensor using the same sensor system requires an auxiliary sensing electrode that contains NH_4^+ ions. It is important for the

sensor to exhibit high stability against water vapor as well as thermal stability because water vapor is generally present with NH_3 gas in varying proportion. Recently, we have proposed solid electrolyte type NH_3 gas sensors based on the $(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3$ solid electrolyte with a rare-earth ammonium sulfate double salt $\text{R}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4$ (R = rare-earths)^{9,10)} or the lanthanum oxysulfate based $\text{La}_2\text{O}_2\text{SO}_4\text{-NH}_4\text{H}_2\text{PO}_4$ solid solution^{9,11)} as auxiliary sensing electrodes that have relatively high chemical stability. Although both sensors have high sensitivity that obeys the Nernst equation ($E = C - RT/nF \cdot \ln(P_{\text{NH}_3})$, ($n = 1.00$)) at 230–300 °C or 170–190 °C, respectively, they do not exhibit the theoretical NH_3 gas sensitivity under highly humid conditions with H_2O over 0.6 vol %, because the water durability of these materials is insufficient. In order to realize a stable sensor output electromotive force (EMF), even under highly humidified conditions, it is necessary to select an auxiliary sensing electrode material with extremely high chemical stability.

Among the various types of material that contains NH_4^+ ions, NH_4^+ - β -gallate (NH_4^+ - $\text{Ga}_{11}\text{O}_{17}$)¹²⁾ is considered to be a suitable candidate as an auxiliary sensing electrode with high chemical stability because the NH_4^+ ions in NH_4^+ - $\text{Ga}_{11}\text{O}_{17}$ are stable in the β -gallate type layered structure. Furthermore, NH_4^+ ions migrate within the conduction plane of the NH_4^+ - $\text{Ga}_{11}\text{O}_{17}$ structure, and so high selectivity for NH_3 gas detection is expected.

In this study, a highly water durable NH_3 gas sensor was fabricated by combining the $(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3$ solid electrolyte and NH_4^+ - $\text{Ga}_{11}\text{O}_{17}$ as the auxiliary sensing electrode, and the NH_3 gas sensing properties were investigated under highly humid atmospheric conditions.

2 Experimental

(K^+ , Rb^+)- $\text{Ga}_{11}\text{O}_{17}$ was synthesized by pelletizing a

Fig. 1 Schematic illustration of the proposed NH_3 gas sensor.

mixture of K_2CO_3 , Rb_2CO_3 , and Ga_2O_3 (molar ratio is 1:1:10) followed by calcinations at 1320°C for 2 h in air to synthesize $(\text{K}^+, \text{Rb}^+)\text{-Ga}_{11}\text{O}_{17}$. The pellets were then pulverized, re-pelletized, and further sintered at 1320°C for 6 h in air. $\text{NH}_4^+\text{-Ga}_{11}\text{O}_{17}$ was obtained by the ion-exchange of $(\text{K}^+, \text{Rb}^+)\text{-Ga}_{11}\text{O}_{17}$ in molten NH_4NO_3 at 180°C for 25 days. The obtained $\text{NH}_4^+\text{-Ga}_{11}\text{O}_{17}$ was washed three times with ultrapure water until K^+ , Rb^+ , and NH_4NO_3 were rinsed off.

The $\text{NH}_4^+\text{-Ga}_{11}\text{O}_{17}$ sample obtained was identified by X-ray powder diffraction (XRD) using $\text{Cu K}\alpha$ radiation (Rigaku, Multiflex). Thermal analysis (Shimadzu, DTA-60H) was carried out in a synthetic air atmosphere. The electrical conductivity of $\text{NH}_4^+\text{-Ga}_{11}\text{O}_{17}$ was measured by the complex impedance method in the frequency region from 5 Hz to 13 MHz (Hewlett Packard, Precision LCR meter 8284A) and in the temperature range from 50 to 300°C .

Figure 1 shows a schematic illustration of the NH_3 gas sensor. An Al metal thin film was prepared as a reference electrode on one side of an Al^{3+} ion conducting solid electrolyte $(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3$ pellet using a vacuum evaporation system (Jeol, JEE-420). The Al metal was covered with a sputtered Pt film produced using an ion-coater (Eiko, Ion-coater IB-3). The $\text{NH}_4^+\text{-Ga}_{11}\text{O}_{17}$ electrode was set on the opposite side of the electrolyte pellet. Au or Pt net was placed on the sensor element and reference electrode as current collectors, and the sensor was heated to an operating temperature of 230°C .

NH_3 gas concentrations from 200 to 500 ppm were regulated by mixing 1 % NH_3 diluted with N_2 gas and humidified air. The humidified air (0.6–4.2 vol % H_2O) was obtained by passing dry air through H_2O at $0\text{--}30^\circ\text{C}$. The total gas flow rate was kept constant at $100\text{ mL}\cdot\text{min}^{-1}$. The oxygen gas pressure (P_{O_2}) was fixed at $2.1 \times 10^4\text{ Pa}$. The sensor output EMF was monitored with an electrometer (Advantest, R8240).

3 Results and Discussion

XRD measurement confirmed that the diffraction peaks of $\text{NH}_4^+\text{-Ga}_{11}\text{O}_{17}$ were shifted to lower angles than those of $(\text{K}^+, \text{Rb}^+)\text{-Ga}_{11}\text{O}_{17}$. In addition, a weight loss (*ca.* 1.5 wt %) together with an exothermic peak observed by thermal analysis suggested the release of NH_3 from the $\text{NH}_4^+\text{-Ga}_{11}\text{O}_{17}$ solid between $270\text{--}400^\circ\text{C}$, whereas no weight loss was observed for the $(\text{K}^+, \text{Rb}^+)\text{-Ga}_{11}\text{O}_{17}$ solid. These results indicate that the K^+ and Rb^+ ions in $(\text{K}^+, \text{Rb}^+)\text{-Ga}_{11}\text{O}_{17}$ were successfully ion-exchanged with NH_4^+

Fig. 2 Representative sensor response curve for the proposed sensor with a $\text{NH}_4^+\text{-Ga}_{11}\text{O}_{17}$ auxiliary sensing electrode at 230°C . The NH_3 gas concentration was varied from 200 to 500 ppm and vice versa under humidified atmosphere (4.2 vol % H_2O).

ions, and NH_4^+ ions were present in the resultant $\text{NH}_4^+\text{-Ga}_{11}\text{O}_{17}$ solid.

The electrical conductivity of the $\text{NH}_4^+\text{-Ga}_{11}\text{O}_{17}$ solid was measured to determine the temperature suitable for application of the $\text{NH}_4^+\text{-Ga}_{11}\text{O}_{17}$ solid as the auxiliary sensing electrode. The conductivity increased monotonically with the temperature up to 230°C but decreased above 250°C , which indicates that the NH_3 in the $\text{NH}_4^+\text{-Ga}_{11}\text{O}_{17}$ solid starts to be released at *ca.* 250°C . It is essential that the NH_4^+ ions are retained in the auxiliary sensing electrode for NH_3 gas sensing; therefore, the optimum sensor operation temperature was determined to be 230°C , which is 20°C lower than the operating temperature limit, over which NH_4^+ ions are released.

Figure 2 shows a representative sensor response curve observed for variation of the NH_3 gas concentration from 200 to 500 ppm and vice versa at 230°C in a humidified atmosphere (4.2 vol % H_2O). The response time, defined as the time to attain a 90 % total response, was within 6 min (Response time includes the time for substitution of the test gas in the furnace). The sensor output EMFs for increasing and decreasing NH_3 gas concentrations were the same, which confirmed that the sensor with $\text{NH}_4^+\text{-Ga}_{11}\text{O}_{17}$ as the auxiliary sensing electrode exhibits a continuous and reproducible response for change in the NH_3 gas concentration even under highly humid conditions of 4.2 vol % H_2O .

The following plausible reactions are expected to occur at the auxiliary sensing electrode, the interface between the auxiliary sensing electrode and the Al^{3+} ion conducting electrolyte, and at the Al metal thin film reference electrode.

Auxiliary sensing electrode:

Interface between the auxiliary sensing electrode and the $(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3$ electrolyte:

Reference electrode (Al metal thin film):

Fig. 3 The relationship between the sensor output EMF and the logarithm of the NH_3 gas concentration at 230°C in various H_2O content.

From the Eqs. (1) to (3), total chemical reaction can be expressed as follows.

The following Nernst equation can be obtained.

$$E = E_0 - (R/nF)T \cdot \ln \{ (a_{\text{Al}})^{1/3} \cdot (a_{(\text{H}_{0.6}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3})^{19/12} \cdot (P_{\text{NH}_3}) \cdot (a_{\text{NH}_4^+ \cdot \text{Ga}_{11}\text{O}_{17}})^{-1} \cdot (a_{(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3})^{-19/12} \} \quad (5)$$

where, a and P terms that represent the activity of the solid materials and the pressure of the gas, respectively, and R , F , and n are the gas constant, Faraday's constant, and the number of electrons participating in the reaction (here, $n=1.00$). The activities of the solids are constant when the temperature is fixed; therefore, the Nernst equation (Eq. (5)) can be finally simplified as follows.

$$E = C - (RT/nF) \ln (P_{\text{NH}_3}) \quad (C: \text{constant}) \quad (6)$$

Figure 3 depicts the relationship between the sensor output EMF and the logarithm of the ammonia gas concentration at 230°C for a sensor with the $\text{NH}_4^+ \cdot \text{Ga}_{11}\text{O}_{17}$ auxiliary sensing electrode under various humidified atmospheres (0.6, 2.3, and 4.2 vol % H_2O). The theoretical slope ($n=1.00$) estimated from Eq. (6) is also presented as a solid line. The sensor output EMFs decrease linearly with increasing NH_3 concentration and a 1:1 linear relationship is observed between the EMF and the logarithm of the NH_3 gas concentration. The n values calculated from the slope for change in the NH_3 concentrations were 1.03 (0.6 vol % H_2O), 0.98 (2.3 vol % H_2O), and 1.01 (4.2 vol % H_2O), which coincide well with the theoretical value ($n=1.00$), and the sensor output EMFs at every NH_3 concentration are almost the same, regardless of the water vapor content in the gas under test. Furthermore, as shown in Fig. 4, the sensor output EMF

Fig. 4 Deviation in sensor EMF with time upon change of the H_2O content ratio between 0.6 and 4.2 vol % at 230°C .

does not deviate by changing the water content from 0.6 to 4.2 vol % and vice versa. These results provide strong evidence that the present sensor with a $\text{NH}_4^+ \cdot \text{Ga}_{11}\text{O}_{17}$ auxiliary sensing electrode exhibits a theoretical response for change in the NH_3 gas concentration without any interference from water vapor.

4 Conclusion

A novel solid electrolyte type NH_3 gas sensor was fabricated by combining a trivalent Al^{3+} ion conducting solid electrolyte ($(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3$) and $\text{NH}_4^+ \cdot \text{Ga}_{11}\text{O}_{17}$ as the auxiliary sensing electrode. The proposed sensor has sensing performance superior to previously reported NH_3 sensors, and exhibits continuous, quantitative and reproducible response that obeys the theoretical Nernst relationship without any interference from water vapor. The proposed sensor possesses a significant advantage in quantitative NH_3 detection, even in humidified atmosphere, and is therefore expected to be applied as a practical *on-site* NH_3 gas sensing device.

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