— Communication —

Solid Electrolyte Type NH_3 Gas Sensor Applicable in a Humid Atmosphere

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A novel solid electrolyte type ammonia (NH_3) gas sensor was fabricated by the combination of the trivalent aluminum cation conducting solid electrolyte $(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3$ with $\text{La}_2\text{O}_2\text{SO}_4\cdot(\text{NH}_4)_2\text{HPO}_4$ as an auxiliary sensing electrode. Since the present sensor exhibited such a superior sensing performance of theoretical response, which obeys the Nernst relationship between the sensor EMF output and the logarithm of the NH_3 gas concentration along with the stable, continuous, and reproducible response even under humidified condition, it is greatly expected to be applied to a practical NH_3 gas sensing device.

Key Words : Solid Electrolyte, Ammonia Gas Sensor, Ammonium Hydrogen Phosphate, Rare-earth Oxysulfate

1 Introduction

Ammonia is extensively utilized in many chemical industries, fertilizer factories, refrigeration systems, etc. However, its toxicity is so high that exposure of human body in high concentration ammonia gas is hazardous to life. In order to prevent the serious accidents caused by the NH_3 gas leakage, the gas detecting device which can precisely measure the NH_3 gas concentration is required.

Today, instruments based on ion chromatography or gas chromatography are widely used for the NH_3 gas detection because of their high sensitivity to the NH_3 gas down to ppb level. However, they are too expensive and too large to settle the every site where NH_3 gas emitted. Furthermore, since some pretreatment for the sample gas is always necessary, they are not suitable for the *on-site* gas monitoring, and the compact ammonia gas sensing devices which can set at every emitting site are greatly requested.

Until now, many kinds of compact NH_3 gas sensors using semiconductor,^{1,2)} quartz crystal microbalance (QCM),³⁾ organic compounds,⁴⁾ and solid electrolytes^{5,6)} have been proposed. However, these sensors are unsuitable for the *on-site* NH_3 gas monitoring from the view points of gas selectivity, sensitivity, and maintenance free. While the semiconductor and QCM type sensors show a rapid response, they have a disadvantage of low selectivity for the gas detection in contaminated atmosphere, because its gas sensing mechanism is based on the resistance or frequency change by the gas adsorption on the semiconductor or quartz surface. For the sensors using organic compounds, they could not operate at elevated temperatures due to their low thermal stability. On the other hand, solid electrolyte type sensors have advanced merits of both selective and quantitative gas detection based on a unique characteristic of solid electrolyte that only a single ion species can migrate in solids. In addition, since the components of the sensor are all solid materials, we can fabricate a compact sen-

sor. Therefore, the solid electrolyte type sensor is expected to be a practical candidate for the accurate NH_3 gas detection.

In our previous studies on the solid electrolyte type gas sensors⁷⁻⁹⁾ with the Al^{3+} ion conducting solid electrolyte of $(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3$ ^{10,11)} as the sensor component, we have successfully developed the CO_2 ,⁷⁾ NO_x ,⁸⁾ and SO_2 gas sensors⁹⁾ possessing the excellent sensing performance such as high selectivity and long term stability. Although we have also developed a NH_3 gas sensor,¹²⁾ which can exactly detect the NH_3 gas concentration at 230 °C, by combining the $(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3$ solid electrolyte and rare earth ammonium sulfate of $\text{R}_2(\text{SO}_4)_3\cdot(\text{NH}_4)_2\text{SO}_4$ ¹³⁾ (R = Pr, Nd) as the auxiliary sensing electrode, the sensor EMF was influenced by the water vapor due to low water-resistant property of the $\text{R}_2(\text{SO}_4)_3\cdot(\text{NH}_4)_2\text{SO}_4$ solid. For realizing the high NH_3 gas sensing performance even under humidified condition, water-durable ammonia salt is demanded for auxiliary sensing electrode. One of the promising approaches to enhance water durability of auxiliary sensing electrode is to mix ammonium salt with water-proof material.

In this communication, we have developed a water-durable auxiliary sensing electrode by mixing ammonium hydro phosphate $(\text{NH}_4)_2\text{HPO}_4$ with lanthanum oxysulfate $\text{La}_2\text{O}_2\text{SO}_4$ which have high durability for water, and investigated the NH_3 gas sensing properties of the sensor based on the $(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3$ with the $\text{La}_2\text{O}_2\text{SO}_4\cdot(\text{NH}_4)_2\text{HPO}_4$ solid as an auxiliary sensing electrode.

2 Experimental

$\text{La}_2\text{O}_2\text{SO}_4$ was prepared by heating La_2S_3 at 900 °C for 12 h in air. The $\text{La}_2\text{O}_2\text{SO}_4$ obtained and $(\text{NH}_4)_2\text{HPO}_4$ are mixed in a molar ratio of 7 : 3 in an agent pot at a rotation speed of 300 rpm for 4 h with a planetary ball milling apparatus. The mixed powder was pelletized and sintered at 190 °C for 10 h in air.

Fig. 1 Over-view of the present NH_3 gas sensor.

The samples obtained were identified by X-ray powder diffraction (XRD) with Cu-K α radiation (Rigaku, Multiflex). The electrical conductivity of $0.7\text{La}_2\text{O}_2\text{SO}_4\cdot 0.3(\text{NH}_4)_2\text{HPO}_4$ was measured by a complex impedance method at the frequency region from 5 Hz to 13 MHz (Hewlett Packard, Precision LCR meter 8284A) in the temperature range from 50 to 300 °C.

Figure 1 illustrates the over-view of the NH_3 gas sensor. As a reference electrode, aluminum metal thin film was prepared on one side of Al^{3+} ion conducting solid electrolyte ($(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3$) pellet by the vacuum evaporation system (JEOL, JEE-420) and then the Al metal was covered with Pt sputtered film with the ion-coater (Eiko, ion-coater IB-3). The $0.7\text{La}_2\text{O}_2\text{SO}_4\cdot 0.3(\text{NH}_4)_2\text{HPO}_4$ electrode was set on the opposite side of Al^{3+} ion conducting solid. After Pt or Au nets were applied as the electrodes to get a good electrical contact, the sensor element was set in an electric furnace and heated up to the operating temperature of 190 °C.

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

3 Results and Discussion

From the XRD measurement of the $0.7\text{La}_2\text{O}_2\text{SO}_4\cdot 0.3(\text{NH}_4)_2\text{HPO}_4$ solid, it was found that the sample has a single phase of the orthorhombic $\text{La}_2\text{O}_2\text{SO}_4$ structure and the crystal lattice of the sample was expanded compared with that of mother $\text{La}_2\text{O}_2\text{SO}_4$, suggesting the formation of the $0.7\text{La}_2\text{O}_2\text{SO}_4\cdot 0.3(\text{NH}_4)_2\text{HPO}_4$ solid solution.

In order to confirm the temperature where the $0.7\text{La}_2\text{O}_2\text{SO}_4\cdot 0.3(\text{NH}_4)_2\text{HPO}_4$ solid can be utilized as the auxiliary sensing electrode, we measured the electrical conductivity of the $0.7\text{La}_2\text{O}_2\text{SO}_4\cdot 0.3(\text{NH}_4)_2\text{HPO}_4$ solid. Figure 2 depicts the temperature dependence of the conductivity for the $0.7\text{La}_2\text{O}_2\text{SO}_4\cdot 0.3(\text{NH}_4)_2\text{HPO}_4$ solid. The conductivity monotonically increased up to 200 °C with increasing the temperature. However, the conductivity steeply decreased above 200 °C, indicating that $\text{NH}_4\text{H}_2\text{PO}_4$ in the $0.7\text{La}_2\text{O}_2\text{SO}_4\cdot 0.3(\text{NH}_4)_2\text{HPO}_4$ solid vaporized at ca. 200 °C. Because it is essential to contain the NH_4^+ ion in

Fig. 2 Temperature dependence of the electrical conductivity for the $0.7\text{La}_2\text{O}_2\text{SO}_4\cdot 0.3(\text{NH}_4)_2\text{HPO}_4$ solid.

Fig. 3 A typical sensor response curve for the present sensor at 190 °C in a wet atmosphere (H_2O : 0.6 vol%).

the auxiliary sensing electrode for the NH_3 gas sensing, we decided the sensor operation temperature at 190 °C.

Figure 3 presents one of the representative sensor response curves observed when the NH_3 gas concentration was varied from 200 to 500 ppm and vice versa at 190 °C in a wet atmosphere. The response time defined as the time to attain a 90% total response was 4-6 minutes. Since the sensor output EMFs in increasing and in decreasing the NH_3 gas concentration were the same, it was clear that the sensor with the $0.7\text{La}_2\text{O}_2\text{SO}_4\cdot 0.3(\text{NH}_4)_2\text{HPO}_4$ solid as the auxiliary sensing electrode showed a reproducible and continuous response for NH_3 gas. Furthermore, similar response curve to that shown in Fig. 3 was observed even in a dry atmosphere.

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

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):

From the eqs. (1) - (3), total chemical reaction is described as follows.

Then, the following Nernst equation can be obtained.

$$E = E_0 - (R/nF)T \cdot \ln\{(a_{\text{Al}})^{1/3} \cdot (a_{(\text{H}_{0.6}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3})^{19/12} \cdot (P_{\text{NH}_3}) \cdot (P_{\text{O}_2})^{1/4} \cdot (a_{\text{H}_4\text{P}_2\text{O}_7})^{1/2} \cdot (a_{\text{NH}_4\text{H}_2\text{PO}_4})^{-1} \cdot (a_{(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3})^{-19/12}\} \quad (5)$$

Here, a and P terms present the activity of the solid materials and the pressure of the gas, respectively, and R , F , and n are the gas constant, the Faraday's constant, and the number of electrons participated in the above reactions (Here, $n = 1.00$). The activities of solids are constant when the temperature is fixed, and oxygen pressure (P_{O_2}) was kept constant at 2.1×10^4 Pa. Therefore, the Nernst equation (eq. (5)) can be finally simplified as follows.

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

Fig. 4 The relationship between the sensor EMF output and the logarithm of the NH_3 gas concentration at 190°C in a wet (●) and in a dry (□) atmosphere.

Figure 4 depicts the relationship between the sensor EMF output and the logarithm of the ammonia gas concentration at 190°C for the sensor with the $0.7\text{La}_2\text{O}_3\text{SO}_4\text{-}0.3(\text{NH}_4)_2\text{HPO}_4$ auxiliary sensing electrode. The theoretical slope ($n = 1.00$) estimated from the eq. (6) is also shown as a solid line. The n values obtained from the slope for changing the NH_3 gas concentration were 1.00 and 0.97 in a wet and a dry atmosphere, respectively, which are well coincided with the theoretical value of $n = 1.00$, indicating that the present sensor with the $0.7\text{La}_2\text{O}_3\text{SO}_4\text{-}0.3(\text{NH}_4)_2\text{HPO}_4$ auxiliary sensing electrode shows the theoretical response for NH_3 detection with obeying the Nernst equation. Moreover, since the sensor EMF outputs under wet and dry conditions are almost the same at every NH_3 concentration, the present sensor with the $0.7\text{La}_2\text{O}_3\text{SO}_4\text{-}0.3(\text{NH}_4)_2\text{HPO}_4$ auxiliary sensing electrode can detect NH_3 gas even in a wet atmosphere.

4 Conclusion

A new solid electrolyte type NH_3 gas sensor was fabricated by using the trivalent Al^{3+} ion conducting solid electrolyte of $(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3$ with $0.7\text{La}_2\text{O}_3\text{SO}_4\text{-}0.3(\text{NH}_4)_2\text{HPO}_4$ solid as the auxiliary sensing electrode. Since the present sensor shows such a high sensing performance of continuous, quantitative and reproducible response with obeying the theoretical Nernst relationship even under humidified condition, it is greatly expected to be a suitable candidate for *on-site* NH_3 gas sensing device.

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