

Highly Water Durable NH₃ Gas Sensor Based on Al³⁺ Ion Conducting Solid Electrolyte with NH₄⁺-gallate

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Abstract:

A water durable ammonia gas sensor was fabricated by combining Al³⁺ ion conducting solid electrolyte ((Al_{0.2}Zr_{0.8})_{20/19}Nb(PO₄)₃) with NH₄⁺-β-gallate (NH₄⁺-Ga₁₁O₁₇) as the auxiliary sensing electrode and its NH₃ gas sensing performance was investigated in humid atmospheres. The sensor exhibited advanced sensing performance with a continuous, quantitative and reproducible response that obeys the theoretical Nernst relationship even in a highly humidified atmosphere containing 4.2 vol.% H₂O at 230 °C. This superior sensing performance of the proposed sensor in a humid atmosphere should offer to be a practical on-site NH₃ gas sensing tool.

Key words: Ammonia, Solid electrolyte, Aluminum ion conducting solid, Ammonium gallate

Introduction

Ammonia (NH₃) gas is one of the useful gas species in the industrial field. However, NH₃ gas is very toxic and the NH₃ gas sensor showing an exact gas detection with a rapid response is greatly required for preventing serious accidents. Today, although NH₃ gas concentration is detected by using analytical apparatuses based on ion or gas chromatography, these are not suitable for on-site NH₃ gas sensing tool because some pretreatment of sample gas is always required. Furthermore, such equipment is too expensive and too large to install at every NH₃ emission site. Therefore, it is required to develop a smart ammonia gas sensor realizing on-site monitoring at various emission sites. Furthermore, there is a critical problem to solve for accurate NH₃ sensing, that is, the interference of water vapor because NH₃ is usually present together with H₂O.

Until now, various solid electrolyte type NH₃ gas sensors have been proposed [1-3]. However, a practical NH₃ sensor with highly selective and quantitative detection in humid atmospheres has not yet been developed.

Recently, we have proposed the solid electrolyte type NH₃ gas sensors [4, 5] applying the Al³⁺ ion conducting (Al_{0.2}Zr_{0.8})_{20/19}Nb(PO₄)₃ solid electrolyte [6] with rare-earth ammonium sulfate of R₂(SO₄)₃·(NH₄)₂SO₄ (R: rare-earths) [7] or lanthanum oxysulfate based La₂O₂SO₄-NH₄H₂PO₄ solid solution as the auxiliary

sensing electrode. Although both sensors exhibited high sensing performances for NH₃ gas obeying Nernst relationship at 230–300 °C or 170–200 °C, respectively, the theoretical NH₃ gas sensing performance was not realized under high humid atmosphere containing H₂O over 0.6 vol.% due to insufficient water durability of these materials.

In this study, we fabricated a NH₃ gas sensor based on the (Al_{0.2}Zr_{0.8})_{20/19}Nb(PO₄)₃ solid electrolyte combined with NH₄⁺-β-gallate (NH₄⁺-Ga₁₁O₁₇) solid [8] as the auxiliary sensing electrode, and its NH₃ gas sensing performance was investigated under high humid atmospheres [9].

Experimental

NH₄⁺-Ga₁₁O₁₇ was obtained by the ion-exchange method using (K⁺, Rb⁺)-Ga₁₁O₁₇ solid. (K⁺, Rb⁺)-Ga₁₁O₁₇ was prepared from the starting materials of K₂CO₃, Rb₂CO₃, and Ga₂O₃ (molar ratio is 1:1:10). After mixing these powders, the mixture was calcined at 1320 °C for 2 h in air. The K⁺ and Rb⁺ ions in the (K⁺, Rb⁺)-Ga₁₁O₁₇ solid was ionically exchanged to NH₄⁺ ions in molten NH₄NO₃ at 180 °C for 25 days. The obtained NH₄⁺-Ga₁₁O₁₇ was washed three times with ultrapure water until K⁺, Rb⁺, and NH₄NO₃ were rinsed off.

Figure 1 illustrates a schematic illustration of the present NH₃ gas sensor. Aluminum metal thin film was prepared on one side of Al³⁺ ion conducting solid electrolyte pellet [6] as a reference electrode, and the Al metal was

covered with Pt sputtered film to prevent oxidation of Al. The $\text{NH}_4^+\text{-Ga}_{11}\text{O}_{17}$ auxiliary sensing electrode was set on the opposite side of Al^{3+} ion conductor.

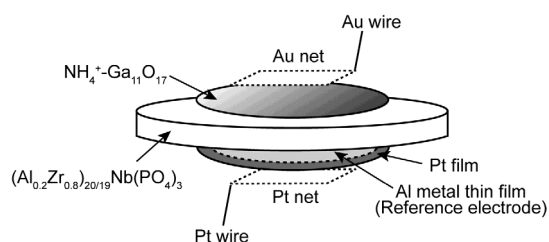


Fig. 1: Schematic illustration of the sensor with $(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3$ and $\text{NH}_4^+\text{-Ga}_{11}\text{O}_{17}$.

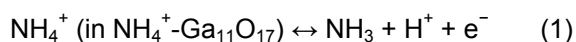
NH_3 gas sensing properties were investigated in the atmosphere where NH_3 gas concentration was regulated by mixing 1% NH_3 diluted with N_2 gas and humidified air. The humidified air (0.6–4.2 vol% H_2O) was obtained by passing dry air through H_2O at 0–30 °C. The total gas flow rate was kept constant 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).

Results and Discussion

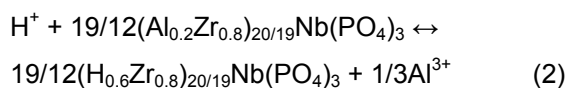
In order to confirm the temperature where the $\text{NH}_4^+\text{-Ga}_{11}\text{O}_{17}$ solid can be used as the auxiliary sensing electrode, the electrical conductivity of the $\text{NH}_4^+\text{-Ga}_{11}\text{O}_{17}$ solid was measured. The conductivity increased monotonically with temperature up to 230 °C, whereas the slight decrease in conductivity was observed at 250 °C. This result 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. Since it is essential to contain NH_4^+ ion in the auxiliary sensing electrode for the stable NH_3 gas sensing, we decided the sensor operation temperature at 230 °C.

For the present sensor, the following plausible reactions are considered to occur at the auxiliary sensing electrode, the interface between the auxiliary sensing electrode and the Al^{3+} ion conductor, and at the Al metal reference electrode.

At auxiliary sensing electrode:



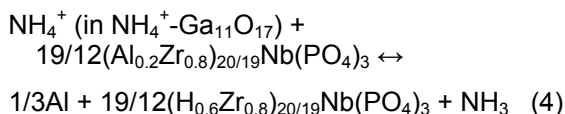
At interface between the auxiliary sensing electrode and the $(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{PO}_4)_3$ electrolyte:



At reference electrode (Al metal thin film):



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



The following Nernst equation can be obtained.

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

where, a and P terms are 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, $n = 1.00$). Since the activities of the solids are constant at fixed temperature, the Nernst equation (Eq. (5)) can be simplified as follows.

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

Figure 2(a) shows the relationship between the sensor output EMF and the logarithm of the NH_3 concentration at 230 °C under various humid atmospheres (H_2O : 0.6, 2.3 and 4.2 vol.%) with the representative sensor response curve observed when the NH_3 gas concentration was varied from 200 to 500 ppm and vice versa (H_2O : 4.2 vol.%). The response time to attain a 90% total response was within 6 minutes (Response time includes substitution time of test gas in the gas flow line), and a continuous and reproducible response was obtained. It was found that the sensor output EMFs decreased with increasing the NH_3 concentration and 1:1 linear relationship was clearly observed between the sensor output EMF and the logarithm of the NH_3 concentration. The electron number (n) participates in the gas sensing, which is calculated from the slope of the EMF change, were 1.03 (H_2O : 0.6 vol.%), 0.98 (H_2O : 2.3 vol.%), and 1.01 (H_2O : 4.2 vol.%), respectively. These values are corresponded well with the theoretical one ($n = 1.00$) estimated from the theoretical Nernst equation (Eq. (6)). Furthermore, the sensor output EMFs at every NH_3 gas concentration are almost the same regardless of the water vapor content in the measuring gas. In addition, the sensor EMF output for 200 ppm NH_3 did not show any meaningful deviation when the water vapor content was varied between 0.6 and 4.2 vol.% as depicted in Fig. 2(b). These results strongly indicate that the present sensor with the $\text{NH}_4^+\text{-Ga}_{11}\text{O}_{17}$ auxiliary sensing electrode can detect NH_3 gas theoretically without the interference of

water vapor, because NH_4^+ ion in the β -gallate structure would be stably hold between the spinel blocks.

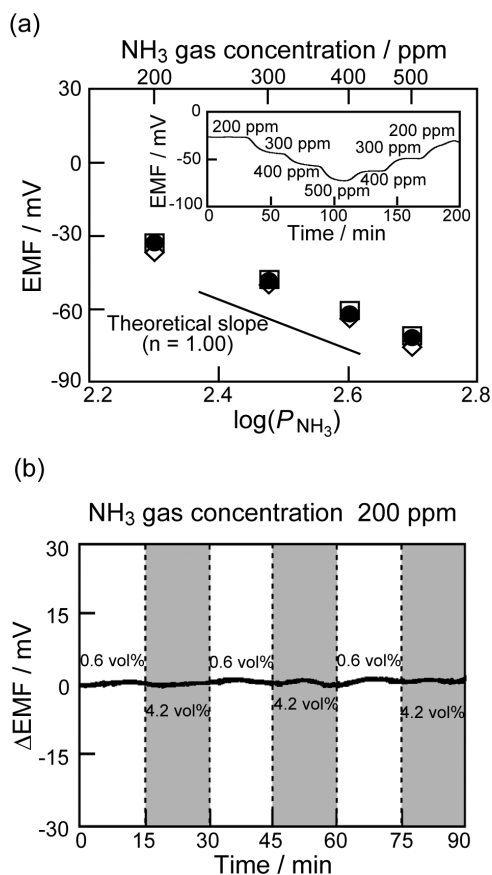


Fig. 2: (a): Relationship between the sensor output EMF and the logarithm of the NH_3 gas concentration at 230 °C in various wet atmospheres (H_2O : 0.6 vol.% (\diamond), 2.3 vol.% (\square), 4.2 vol.% (\bullet)). A typical sensor response curve under wet condition (H_2O : 4.2 vol.%) is also inserted.

(b): Sensor output EMF deviation for 200 ppm NH_3 when the water vapor content was varied between 0.6 and 4.2 vol.%.

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References

- [1] N. Miura and W.L. Worrell, *Chem. Lett.*, **16**, 319-322 (1987). doi:10.1246/cl.1987.319
- [2] N. Imanaka, S. Tamura, and G. Adachi, *Electrochem. Solid-State Lett.*, **1**, 282-284 (1998). doi:10.1149/1.1390713
- [3] N. Imanaka, S. Yoshikawa, T. Yamamoto, and G. Adachi, *Electrochem. Solid-State Lett.*, **2**, 352-355 (1999). doi:10.1149/1.1390834

- [4] T. Nagai, S. Tamura, N. Imanaka, *Sens. Lett.*, **9**, 552-556 (2011); doi:10.1166/sl.2011.1511
- [5] T. Nagai, S. Tamura, N. Imanaka, *Sens. Actuators B*, **147**, 735-740 (2010); doi: 10.1016/j.snb.2010.03.093
- [6] N. Imanaka, Y. Hasegawa, M. Yamaguchi, M. Itaya, S. Tamura, G. Adachi, *Chem. Mater.*, **14**, 4481-4483 (2002); doi: 10.1021/cm020667f
- [7] L.D. Iskhakove, I.E. Sukhova, O.P. Chernova, I.V. Shakhno, V.E. Plyushchev, *Russ. J. Inorg. Chem.*, **20**, 193-196 (1975).
- [8] H. Ikawa, T. Tsurumi, K. Urabe, S. Udagawa, *Solid State Ionics*, **20**, 1-8 (1986); doi:10.1016/0167-2738(86)90027-5
- [9] T. Nagai, S. Tamura, N. Imanaka, *Electrochemistry*, **79**(6), 450-452 (2011)