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 ((Al0.2Zr0.8)20/19Nb(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 (Al0.2Zr0.8)20/19Nb(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 (Al0.2Zr0.8)20/19Nb(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 NH$_4^+$-Ga$_{11}$O$_{17}$ auxiliary sensing electrode was set on the opposite side of Al$^{3+}$ ion conductor.

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$_2$O) was obtained by passing dry air through H$_2$O at 0–30 °C. The total gas flow rate was kept constant at 100 ml·min$^{-1}$. The oxygen gas pressure ($P_{O_2}$) was fixed at 2.1 × 10$^4$ Pa.

The sensor output EMF was monitored with an electrometer (Advantest, R8240).

Results and Discussion

In order to confirm the temperature where the NH$_4^+$-Ga$_{11}$O$_{17}$ solid can be used as the auxiliary sensing electrode, the electrical conductivity of the NH$_4^+$-Ga$_{11}$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 NH$_4^+$-Ga$_{11}$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:

\[
\text{NH}_4^+ (\text{in NH}_4^+-\text{Ga}_{11}\text{O}_{17}) \leftrightarrow \text{NH}_3 + \text{H}^+ + e^- \quad (1)
\]

At interface between the auxiliary sensing electrode and the (Al$_{0.2}$Zr$_{0.8}$)$_{20/19}$Nb(P0$_4$)$_3$ electrolyte:

\[
\text{H}^+ + 19/12(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{P}0_4)_3 \leftrightarrow 1/3\text{Al}^{3+} + 19/12(\text{H}_0.6\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{P}0_4)_3 + \text{NH}_3 \quad (2)
\]

At reference electrode (Al metal thin film):

\[
1/3\text{Al}^{3+} + e^- \leftrightarrow 1/3\text{Al} \quad (3)
\]

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

\[
\text{NH}_4^+ (\text{in NH}_4^+-\text{Ga}_{11}\text{O}_{17}) + 19/12(\text{Al}_{0.2}\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{P}0_4)_3 \leftrightarrow 1/3\text{Al} + 19/12(\text{H}_0.6\text{Zr}_{0.8})_{20/19}\text{Nb}(\text{P}0_4)_3 + \text{NH}_3 \quad (4)
\]

The following Nernst equation can be obtained.

\[
E = E_0 - \frac{RT}{nF} \ln \left( \frac{a_{\text{Al}}^{1/3} \cdot \left( \frac{a_{\text{H}_0.6\text{Zr}_{0.8}}}{a_{\text{Al}_{0.2}\text{Zr}_{0.8}}^{19/12}} \right)^{19/12} \cdot \left( \frac{P_{\text{NH}_3}}{a_{\text{NH}_4^+-\text{Ga}_{11}\text{O}_{17}}} \right)^{-1}}{1} \right) \quad (5)
\]

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.

\[
E = C - \frac{RT}{nF} \ln \left( \frac{P_{\text{NH}_3}}{a_{\text{NH}_4^+-\text{Ga}_{11}\text{O}_{17}}} \right) \quad (6)
\]

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$_2$O: 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$_2$O: 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$_2$O: 0.6 vol.%), 0.98 (H$_2$O: 2.3 vol.%), and 1.01 (H$_2$O: 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 indicates that the present sensor with the NH$_4^+$-Ga$_{11}$O$_{17}$ auxiliary sensing electrode can detect NH$_3$ gas theoretically without the interference of...
water vapor, because \(\text{NH}_4^+\) ion in the \(\beta\)-gallate structure would be stably hold between the spinel blocks.

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**References**


