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NASICON-based NO_2 device attached with metal oxide and nitrite compound for the low temperature operation

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Abstract

NASICON ($Na_3Zr_2Si_2PO_{12}$)-based potentiometric NO_2 devices, such as Au-attached, (ITO, $NaNO_2$)-attached and (ITO, $NaNO_2$–Li_2CO_3)-attached types, were fabricated and their NO_2 sensing properties were investigated in the range of 2–7 ppm NO_2 under 1–50% relative humidity (RH) between 30 °C and 150 °C. The Au-attached device had a NO_2 sensing capability under wet condition (30% RH) without an auxiliary phase, although it showed no EMF response under dry condition (below 1% RH). This result suggests that NO_2 sensing reaction of the device is closely related with water vapor. To enlarge the NO_2 sensitivity at room temperature, a (metal, nitrite)-attached device was fabricated by combining ITO with $NaNO_2$. The EMF change of the (ITO, $NaNO_2$)-attached device was estimated to be 43.6 mV under 30% RH in the range of 2–7 ppm NO_2 and enlarged remarkably in comparison with 17.7 mV of the Au-attached device. However, the NO_2 sensitivity of the (ITO, $NaNO_2$)-attached device was not only fluctuated by the change of relative humidity, but the EMF values shifted upward with increasing humidity at a fixed NO_2 concentration. It is considered that this originates from the fact that a nitrite auxiliary phase is easy to dissolve in water. Therefore, Li_2CO_3 with durability to water vapor was melted together with $NaNO_2$ and used as the auxiliary phase of the (ITO, $NaNO_2$)-attached device. As the result, it was found that the EMF change of the (ITO, $NaNO_2$–Li_2CO_3)-attached device was constant almost without depending on humidity. The EMF values of the device were also proportional to the logarithm of NO_2 concentration and well consistent with theoretical values obtained from the Nernstian equation.

Keywords: NO_2 device; NASICON; $NaNO_2$; ITO

1. Introduction

The NO_x (NO and NO_2) concentration in the atmosphere has been generally measured by spectroscopic instruments based on chemical luminescence and infrared absorption. These apparatuses, however, are not only expensive, but also inapplicable to determination of the NO_x concentration because of its maintenance and time-consuming sampling. In contrast, gas sensors using ceramics surpass them in gas sensing properties such as gas sensitivity, response time and long-term stability, in addition to maintenance and commercial price. Especially, potentiometric NO_x devices using solid-state electrolyte attached with a nitrate or a nitrite compound ($NaNO_3$, $NaNO_2$–Li_2CO_3 and so on) have been attracted a great deal of attention from viewpoint of their practical use [1–12]. This type device has a high selectivity, because it detects an objective gas from the electrochemical reaction. Usually, the potentiometric NO_x device must be operated at elevated temperature (above 150 °C) to advance the electrochemical reaction smoothly. This means that the potentiometric NO_x device contains a weak point should be improved in consumption electric power. Also the devices combined with a heating element have difficulties in downsizing. If the NO_2 sensing at room temperature becomes available, the heater can be eliminated from the sensor system, so that the sensor can be manufactured much smaller and simpler, and operated easily with an electric cell.

Recently, it has been reported that the solid-state electrolyte devices attached with a metal oxide (Sb-doped SnO_2, In_2O_3, ITO: indium tin oxide) and a metal carbonate (Na_2CO_3 and Li_2CO_3–$BaCO_3$) exhibit CO_2 sensing capability even at room temperature [13–16]. The large advantage of the solid-state electrolyte device is to be able to detect target gas by choosing a metallic salt as an auxiliary phase [17,18]. Accordingly, it is conceivable that a solid-state electrolyte device attached with a metal

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oxide and a nitrite can detect NO_2 gas even at room temperature in ambient atmosphere. In the present study, we have studied the NO_2 sensing properties of a NASICON ($Na_3Zr_2Si_2PO_{12}$: Na^+ super ionic conductor)-based potentiometric device using ITO and nitrite compounds ($NaNO_2$, $NaNO_2$–Li_2CO_3) in detail and proposed the NO_2 sensing mechanism of the device based on experimental informations.

2. Experimental

2.1. Materials preparation

NASICON ($Na_3Zr_2Si_2PO_{12}$: Na^+ super ionic conductor) as a solid electrolyte were prepared by a sol–gel technique using $Si(OC_2H_5)_4$, $Zr(OC_4H_9)_4$, $PO(OC_4H_9)_3$ and $NaOC_2H_5$. These alkoxides were stoichiometrically dissolved in an ethanol solvent containing HNO_3 and allowed to stand about 20 h under stirring. This operation was carried out in a dry N_2 atmosphere and the ethanol solvent was kept at 60 °C. Then, the distilled water was added to the ethanol solution for the hydrolysis. The resulting precipitates were dried at 120 °C in air for 24 h. After calcined at 750 °C in air for 1 h, the precursor powders were compacted into a disk (9 mm in diameter and 1.2 mm thick). The disk was sintered at 1200 °C in air for 5 h and polished with a sand paper. As previously reported, ITO (Sn-doped In_2O_3) was chosen as a metal oxide because the CO_2 device using ITO as a sensing material showed excellent sensing capabilities even at room temperature [15]. Ten atomic percent Sn-doped In_2O_3 powders were conventionally prepared from an aqueous mixed solution of $InCl_3$ and $SnCl_4$. Then, the powders were calcined at 1000 °C in air for 5 h. A nitrite compound was synthesized by calcining a mixture of $NaNO_2$ and Li_2CO_3 powders (9:1 in molar ratio) at 360 °C in air for 10 min.

2.2. Fabrication of NO_2 sensing device

Two types of devices were fabricated by combining NASICON disks with sensing electrode materials, such as Au, ITO and an auxiliary phase ($NaNO_2$ or $NaNO_2$–Li_2CO_3), as schematically drawn in Fig. 1. To fabricate Au-attached type device (type-A), both of the counter and the sensing electrodes were constructed by using a gold paste, followed by calcination at 800 °C in air for 2 h (Fig. 1(a)). A device of type-A without an auxiliary phase was called type-A1, while a $NaNO_2$-attached one called type-A2. For an (Au, $NaNO_2$)-attached device (type-A2), a $NaNO_2$ paste mixed with ethyleneglycol was applied on the top of the sensing electrode (Au). For an ITO-attached type device (type-B), the counter electrode (Au) was prepared in the same manner, while the sensing electrode of the device was formed by applying ITO powders assisted with a nitrite compound as the auxiliary phase (Fig. 1(b)). For a type B, ITO-attached device without an auxiliary phase was called type-B1. Furthermore, ITO-attached devices were constructed by using nitrite compounds, such as $NaNO_2$ and $NaNO_2$–Li_2CO_3, which were called type-B2 or type-B3, respectively. The attachment of sensing electrode was carried out by calcining the whole assembly at 320 °C in air for 5 min. The counter electrode was covered with a protective layer (an inorganic adhesive) to isolate from water vapor and NO_2 in atmosphere.

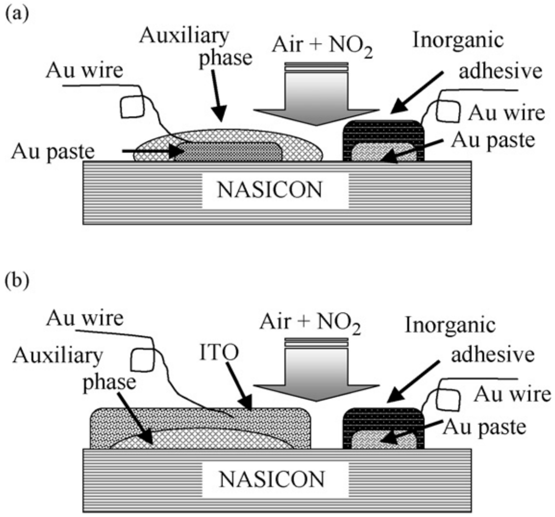

Fig. 1. Schematic drawing of NO_2 devices: (a) Au-attached type (type-A) and (b) ITO-attached type (type-B).

2.3. Measurement of NO_2 sensing properties

Gas sensing properties of the NASICON-based device were measured in a conventional gas-flow apparatus equipped with a heating facility in the temperature range of 30–150 °C. Sample gases consisting of air, NO_2 and H_2O were prepared by diluting a parent NO_2 gas (10 ppm NO_2 in dry synthetic air) with wet and/or dry synthetic air. The wet air was prepared by allowing the dry air to bubble through water. The concentration of NO_2 and relative humidity (RH) in the sample gas were varied in the range of 2–7 ppm NO_2 and of 1–50% RH, respectively. The sample gases let to flow over the sensing electrode at a rate of 0.1 dm^3/min. The electromotive force (EMF) of the sensing device was measured with a digital electrometer.

3. Results and discussion

3.1. NO_2 sensing properties of the devices

3.1.1. Au-attached type (type-A)

In potentiometric NO_2 devices using a solid-state electrolyte, an auxiliary phase, such as a nitrite or a nitrate, is inevitable to form an NO_2 sensing interface in combination with a sensing electrode. The Au-attached device (type-A1) was firstly fabricated without an auxiliary phase and the gas sensing properties to NO_2 were examined. Fig. 2(a) shows the EMF response transients of type-A1 to variations in NO_2 concentration under 30% RH at 30 °C. When NO_2 concentration was changed from 2 ppm to 3 ppm in a measuring chamber, the EMF change ($\Delta EMF'_{NO_2}$) was 4.3 mV. Here $\Delta EMF'_{NO_2}$ stands for the increments in EMF on increasing the NO_2 concentration from 2 ppm to 3 ppm. The EMF change became large as the NO_2 concentration increased from 2 ppm to 7 ppm and finally reached up to 17.7 mV. Each 90% response time to stepwise changing NO_2 concentration was