ELSEVIER

Ceramics International 27 (2001) 191–194

CERAMICS INTERNATIONAL

Potentiometric NO_2 gas sensor using $LiRESiO_4$ (RE = Nd and Sm)

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Received 3 January 2000; received in revised form 26 February 2000; accepted 29 March 2000

Abstract

The properties of two kinds of lithium ionic conductors, $LiNdSiO_4$ and $LiSmSiO_4$ as solid electrolytes were investigated by designing the solid electrochemical cells such as (−) air, Pt|lithium ionic conductor|Au, $LiNO_3$, NO_2, O_2 (+), for the NO_2 gas sensor. The electromotive force, EMF, of these sensors increased linearly with an increase in the logarithmic value of nitrogen dioxide partial pressure, in accordance with Nernst's law. It was suggested from the slope of Nernst's equation that the one-electron reaction associated with the nitrogen dioxide molecule takes place at the detection electrode around 150°C. The 90% response time of EMF for an increase in NO_2 concentration were within 12 min at 150°C.

Keywords: C. Electrical properties; D. Apatite; D. Silicate; E. Sensors

1. Introduction

Recently, the combination of certain ionic conductive films and solid electrodes has made it possible to develop the gas sensors. The application of the solid electrolytes in this area have been extensively studied. For instance, there have been a number of NO_2 gas sensors, where β-alumina (Na-β-Al_2O_3) or Nasicon ($Na_3Zr_2Si_2PO_{12}$) is used as the solid electrolyte and $NaNO_3$ as the solid electrode [1–3]. However, this type of gas sensors has not been put to practical use to date. Consequently, the development of NO_2 gas sensors with high sensitivity, good selectivity, rapid response time, good long-term stability and high accuracy is required.

Generally, dense ionic conductors are desirable for the development of chemical sensor materials. As the result of the screening process for well-compacted conductive alkali–metal ion solid electrolytes, we reported that $LiNdSiO_4$ and $LiSmSiO_4$ are dense [4, 5]. According to Sato et al., $LiLnSiO_4$ (Ln = La, Nd, Sm, Eu, Gd and Dy) is the mixture of $Li_xLn_{10-x}Si_6O_{24}O_{3-x}$ ($1 \leqslant x \leqslant 3$) with apatite structure and an amorphous phase including some kinds of lithium silicate glass phases [6]. The high density of these lithium ionic conductors may be due to the fact that the sintering process progresses well due to the existence of minor components as binders in the grain boundary. In this work, electrical properties of these two lithium ionic conductors were investigated, along with the response characteristics of the potentiometric NO_2 gas sensors in which each ionic conductor was used as a solid electrolyte.

2. Experimental

The following solid state cell was prepared for the CO_2 sensor:

(−) air, Pt|lithium ionic conductor|Au, $LiNO_3$, NO_2, O_2(+)

The sensor structure is illustrated in Fig.1. Here, ionic conductors used were $LiNdSiO_4$ and $LiSmSiO_4$, which were sintered at 1100°C. Discs of these ionic conductors were prepared, according to the methods previously reported [4,5]. The diameter and thickness of the discs after the sintering were 8 and 2 mm, respectively. After one side of a disc was coated with Pt paste and the other side with Au paste, the disc was baked at 800°C. Pt wires were connected to both sides of the disc. The Au detection electrode was immersed in an aqueous solution of $LiNO_3$ and then dried to prepare the solid electrode. The sensor thus designed was fixed on one end of

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0272-8842/01/$20.00
PII: S0272-8842(00)00062-6

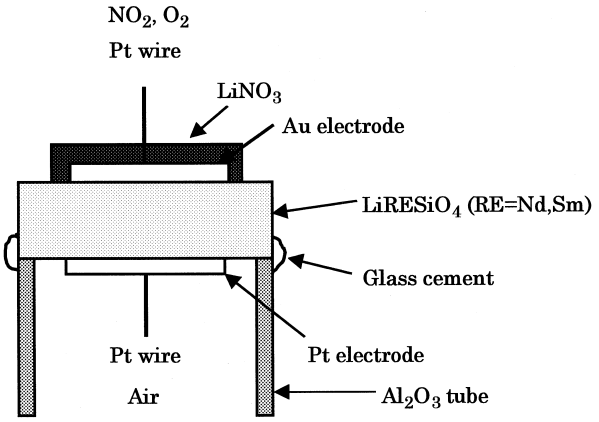

Fig. 1. Schematic view of NO_2 gas sensor.

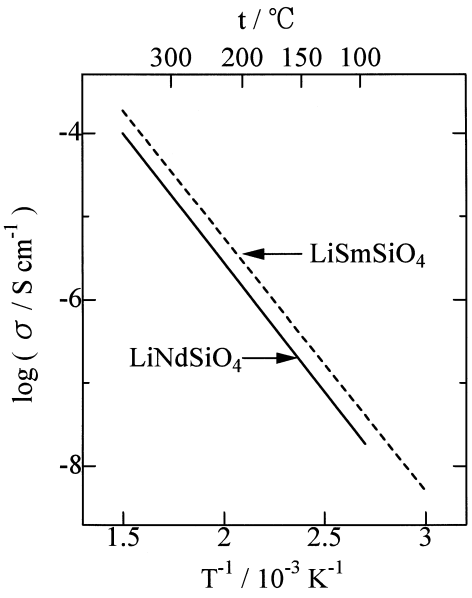

Fig. 2. Temperature dependence of conductivity.

an alumina pipe with a glass cement so that the Pt counter electrode was inside.

The response characteristics were measured as follows: The standard NO_2 gases of 8.8×10^{-1} Pa, 2.2×10^{0} Pa and 8.2×10^{0} Pa prepared by diluting given amounts of NO_2 with synthetic air were purchased from Sumitomo-Seika Inc. These standard gases were passed through the detection electrode side of the sensors at the flow rate of 50 cm^3 min^{-1}. The electromotive force, EMF, of the sensor was measured using a Advantest TR8652 electrometer.

The sintered bulk densities and apparent porosities were determined according to the STS 124 and JIS R 2205. Electrical conductivities were measured with a Yokogawa Hewlett-Packard 4192A multifrequency LCR meter in the frequency range of 100 Hz to 10 MHz and in the temperature range of 50–400°C.

3. Results and discussion

The sintered bulk densities of $LiNdSiO_4$ and $LiSmSiO_4$ were 4.92 and 4.87 g cm^{-3}, respectively. The apparent porosities of these silicates were both 0.4%.

The conductivities in moist air were very close to those in dry both for all of the samples, indicating that these samples are not proton conductors. The current response to a potential change from +1 to −1 V was examined using Pt|lithium ionic conductor|Pt. The current did not decline rapidly after the polarity change but very gradually approached zero, suggesting that ions are responsible for the electrical conduction. Arrhenius plots of total conductivity, σ, are shown in Fig. 2. Here, the σ-values, which are the sum of the conductivity in the grain itself and the conductivity through the grain boundary, were estimated from the results of complex impedance measurements. As can be seen from Fig. 2, conductivities were beyond 3×10^{-8} S cm^{-1} at 100°C for both of the samples, indicating that these samples are sufficiently applicable to the solid electrolyte of the NO_2 gas sensor. Conductivities of samples considered did not change in air for three months.

Figs. 3 and 4 show the dependence of EMF of the NO_2 gas sensors using $LiNdSiO_4$ and $LiSmSiO_4$ on the logarithm of NO_2 partial pressure, $\log P_{NO2}$, in the range of 120–200°C, respectively. The EMF values increase with increasing $\log P_{NO_2}$ for both of the sensors and the dependence of EMF obeys Nernst's equation. In the present apparatus, potentials at a given temperature are almost constant, as the counter electrode is shielded from the detected gas. This indicates that the EMF change occurs from the potential change at the detection electrode and hence the electron transfer number at the detection electrode can be estimated from the slope of the straight lines shown in Figs. 3 and 4. Table 1 summarizes the estimated slopes and electron transfer number, n. Here, the n-value for the sensor using $LiSmSiO_4$ can be approximated as 1 and is almost constant in the range of 120–180°C, suggesting that the detection in the range of 120–180°C is accomplished based on the one-electron transfer reaction associated with NO_2 molecules. On the other hand, the n-value for the sensor using $LiNdSiO_4$ can be approximated as 1 only at 150°C. As can be seen from Table 1, the working temperature region is in the order of $LiNdSiO_4$ < $LiSmSiO_4$ and the working temperature in the low temperature side is in order of the $LiNdSiO_4$ > $LiSmSiO_4$. The stable EMF values for the sensors using $LiNdSiO_4$ and $LiSmSiO_4$ was not obtained below 120 and 100°C, respectively.

From the above results, the following discussion can be made on the response mechanism of the present NO_2 gas sensor. The counter electrode is exposed to the atmosphere in which P_{O2} is always 2.1×10^{4} Pa.

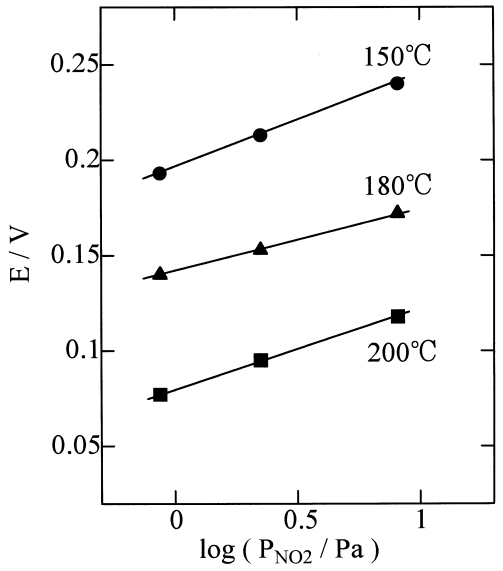

Fig. 3. Dependence of sensor EMF on NO_2 partial pressure in air, (−) air, Pt|$LiNdSiO_4$|Au, $LiNO_3$, NO_2, O_2 (+).

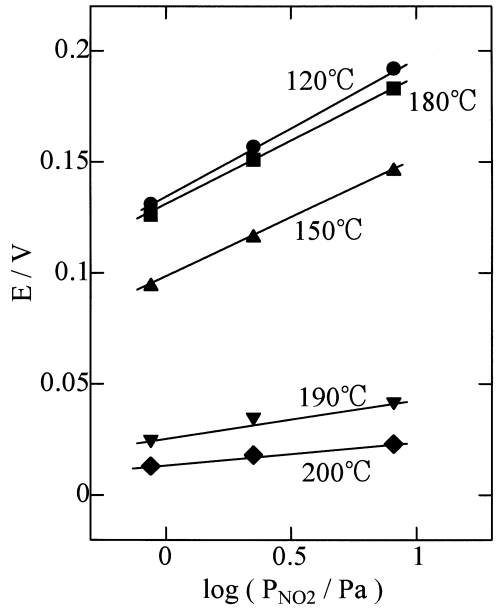

Fig. 4. Dependence of sensor EMF on NO_2 partial pressure in air, (−) air, Pt|$LiSmSiO_4$|Au, $LiNO_3$, NO_2, O_2 (+).

Therefore, the reaction at the counter electrode can be expressed by Eq. (1),

$$Li^+ + 1/4O_2 + e^- = 1/2Li_2O \quad (1)$$

On the other hand, the following reaction is thought to occur at the detection electrode.

$$Li^+ + NO_2 + 1/2O_2 + e^- = LiNO_3 \quad (2)$$

Table 1
Values of slopes of sensor EMF vs. log P_{NO_2} and electron transfer numbers, n

Temperature/°C	Slope/mV decade^{-1}	n
Air Pt|LiNdSiO4|Au LiNO3 NO2 O2		
150	55	1.5
180	33	2.7
200	35	2.7
Air Pt|LiSmSiO4|Au LiNO3 NO2 O2		
120	70	1.1
150	70	1.2
180	60	1.5
190	18	5.3
200	13	7.3

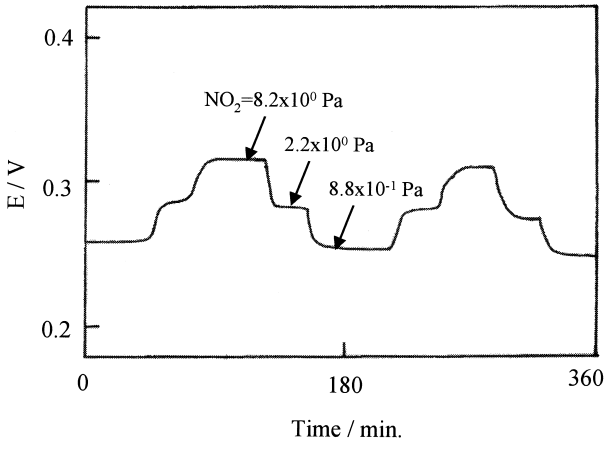

Fig. 5. Response curve of sensor EMF in air at 150°C, (−) air, Pt|$LiSmSiO_4$|Au, $LiNO_3$, NO_2, O_2 (+).

When the Nernst's equation is applied to Eqs. (1) and (2), the following equations are derived as the potential of the counter electrode, Ec, and that of the detection electrode, Es,

$$Ec = Ec' - (RT/F)\ln\left(a_{Li_2O}{}^{1/2}/a_{Li+}\cdot\left(P^{I}_{O_2}\right)^{1/4}\right) \quad (3)$$

$$Es = Es' - (RT/F)\ln\left(a_{LiNO_3}/a_{Li+}\cdot P_{NO_2}\cdot\left(P^{II}_{O_2}\right)^{1/2}\right) \quad (4)$$

where E', a_{Li2O}, a_{LiNO3}, P_{O2} and P_{NO2} are standard electrode potential, activity of Li_2O, activity of $LiNO_3$, O_2 partial pressure and NO_2 partial pressure, respectively, and the other symbols have their usual meanings. Both Ec' and Es' are constants. Therefore, the EMF, E, is expressed as:

$$E = Es - Ec$$

$$= E' - (RT/F)\ln\left(a_{LiNO_3}\cdot\left(P^{I}_{O_2}\right)^{1/4}/a^{1/2}_{Li_2O}\cdot P_{NO_2}\cdot\left(P^{II}_{O_2}\right)^{1/2}\right) \quad (5)$$

where E' is a constant. When the activities of $LiNO_3$, Li_2O, $P^{I}_{O_2}$ and $P^{II}_{O_2}$ are kept constant, the NO_2 concentration can be calculated from E. Undoubtedly, the present results can be explained by this Eq. (5).

Fig. 5 shows the EMF response curve of the sensor prepared using $LiSmSiO_4$ as a solid electrolyte when NO_2 concentration was changed in three steps from 8.8×10^{-1} to 8.2×10^{3} Pa at 150°C. The response time was relatively rapid and the 90% response times for an increase and a decrease of NO_2 concentration were about 12 and 15 min or less, respectively. The sensor prepared using $LiNdSiO_4$ exhibited a response behavior similar to that of a sensor using $LiSmSiO_4$.

4. Conclusion

Lithium ionic conductors, $LiNdSiO_4$ and $LiSmSiO_4$, with conductivities above 3×10^{-8} S cm^{-1} at 100°C were prepared and their effectiveness as solid electrolytes of the potentiometric NO_2 gas sensors was investigated. The one-electron transfer reaction associated with NO_2 molecules were found to occur at the detection electrode around 150°C for both of the sensors. The 90% response times of EMF at 150°C were within 12 min, when the NO_2 concentration was increased.

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