Cl_2 Gas Sensor Using Na^+ Conducting Solid Electrolyte

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A composite Na^+ conductor of polycrystalline NASICON mixed with a glassy Na_2O-Al_2O_3-$4SiO_2$ (40wt%) was used in Cl_2 gas sensor. The probe using the composite electrolyte and a RuO_2+NaCl (1:1) measuring electrode gave rapid EMF changes even for sub-ppm level of Cl_2 gas concentration (below 6 ppm).

In recent years, chlorine-containing exhaust gases have become a serious problem because they cause air pollution and acid rains. The development of solid-state sensors able to measure the Cl_2 exhaust gas concentration is extremely appealing. Sensors using solid electrolytes are demonstrably suitable for the continuous and rapid detection of gases. Up to now, Ag^+-β-alumina, MgO-stabilized zirconia, and chloride Cl^- ionic conductors (such as the $PbCl_2$-KCl and the $BaCl_2$-KCl systems) have been reported as materials for Cl_2 gas sensors.[1-6] However, the response for the sensor using the Ag^+-β-alumina is very slow even for high Cl_2 gas concentration. In the case of the stabilized zirconia, the EMF is influenced by the concentration of O_2 gas. The gas sensors using chlorides can not detect Cl_2 at concentration of lower than 10 ppm because of their poor sinterability and poor stability at high temperatures. Stable alkaline chlorides such as NaCl and KCl show poor ionic conductivity that hinders their use as solid electrolytes. Gas sensors using a highly dense Na^+ ionic conducting ceramic with a stable NaCl containing electrode are expected to be suitable for the detection of low Cl_2 concentrations.

In this study, a composite Na^+ conductor of polycrystalline NASICON and glassy Na_2O-Al_2O_3-$4SiO_2$ (40wt%) was used as a Cl_2 gas sensor using a RuO_2-NaCl measuring electrode.

Stoichiometric mixtures of Na_2CO_3, ZrO_2, SiO_2, and $(NH_4)_2HPO_4$ were heated at 900 ºC for 2 h in a platinum crucible for the preparation of NASICON ($Na_3Zr_2Si_2PO_{12}$). The heated material was ground into fine powders using a ball mill for 2 h in a wet process with methanol. The dried powder was reheated at 900 °C for 2 h and then ball-milled for 4 h. A sodium aluminosilicate glass Na_2O-Al_2O_3-$4SiO_2$ was prepared using Na_2CO_3, Al_2O_3 and SiO_2 powders. The mixture was ball-milled with methanol, then the dried powder was calcined in air for 4 h at 900 °C. The 100:40 wt ratio of NASICON and Na_2O-Al_2O_3-$4SiO_2$ was mixed using the ball-milling for 2 h. The dried mixture was pressed into discs at 1000 kg/cm^2 and then sintered at 1050 °C for 2 h. RuO_2 powder (99.9%) dispersed in methanol as the reference electrode was painted on one side of the discs. A mixture (1:1) of RuO_2 and NaCl dispersed in butyl acetate was pained on the opposite side as the measuring electrode. This electroded disc was fixed at an end of an alumina tube with an inorganic adhesive (Fig. 1).

The prepared element was set in a quartz chamber. To obtain several concentrations of air-balanced Cl_2 gas, a mixture (80:20) of 7.3 ppm Cl_2 gas (balanced with N_2) and O_2 gas was diluted with artificial air (CO_2 < 2 ppm and H_2O < 10 ppm), and it was introduced in contact with the sensing electrode. Air was introduced at a flow rate 100 cm^3/min in contact with the reference electrode.

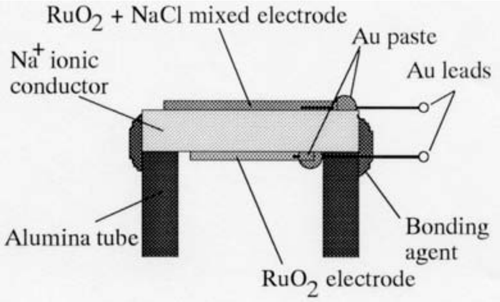

Figure 1. Structure of the sensor probe.

For this sensor, the following two-electron reactions are suggested to occur:

$$\begin{array}{llcll} \text{(Measuring)} & 2Na^+ + Cl_2 + 2e^- & = & 2NaCl & (1) \\ \underline{\text{(Reference)}} & \underline{Na_2O} & \underline{=} & \underline{2Na^+ + (1/2)O_2 + 2e^-} & \underline{(2)} \\ \text{Total} & Na_2O + Cl_2 & = & 2NaCl + (1/2)O_2 & (3) \end{array}$$

The O_2 partial pressure and the activity of Na_2O and NaCl can be considered to be constant. The EMF of the cell is therefore expected to be

$$\mathrm{EMF} = E_o + (RT/nF)\, ln\, [P_{Cl_2}] \qquad (4)$$

where E_o is a constant, R the gas constant, T the absolute temperature, F the Faraday constant, *n* the electron number for the reaction, and P_{Cl2} the concentration of Cl_2.

Highly dense discs of pure NASICON were not obtained even at high sintering temperatures. The mechanical strength and the densification were improved by the addition of a Na_2O-Al_2O_3-$4SiO_2$ glass. X-ray diffraction analysis for the composite samples showed the presence of NASICON phase with ZrO_2 peaks of small intensity. Although the conductivity at 400 °C decreased about one order of magnitude by the glass addition, this dense composite sample possessed conductivity large enough to be used as a solid electrolyte for gas sensors.

Figure 2 shows the typical sensing characteristics at 400 °C (flow rate 200 cm^3/min). On changing the Cl_2 gas concentration, the EMF changed quickly and a steady state value was observed in the high Cl_2 gas concentration region. The 90% response time was about 1~2 min for high Cl_2 gas concentration, and it was prolonged to ca. 10 min for low Cl_2 gas concentration.

Figure 3 shows the Cl_2 concentration dependence of EMF at 400 °C in air. Three samples were tested to confirm the reproducibility of the sensor response. Similar EMF results were obtained for all the samples examined. The measured *n* values were around $n = 1$, lower than the theoretical value $n = 2$.

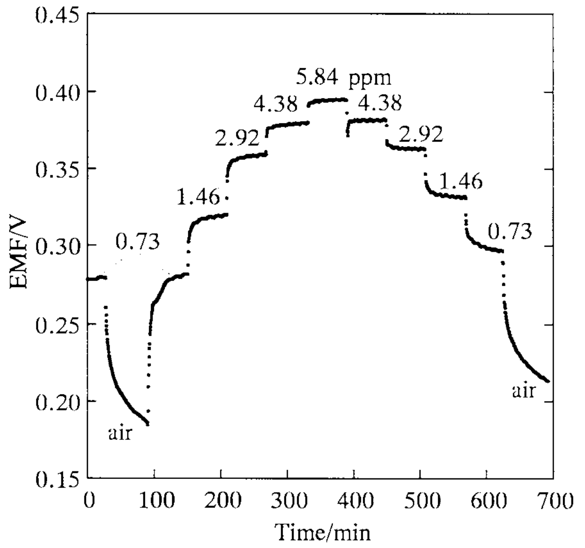

Figure 2. The EMF response at 400 °C of a sensor probe prepared using a NASICON-glass composite electrolyte and a RuO_2-NaCl (1:1) measuring electrode.

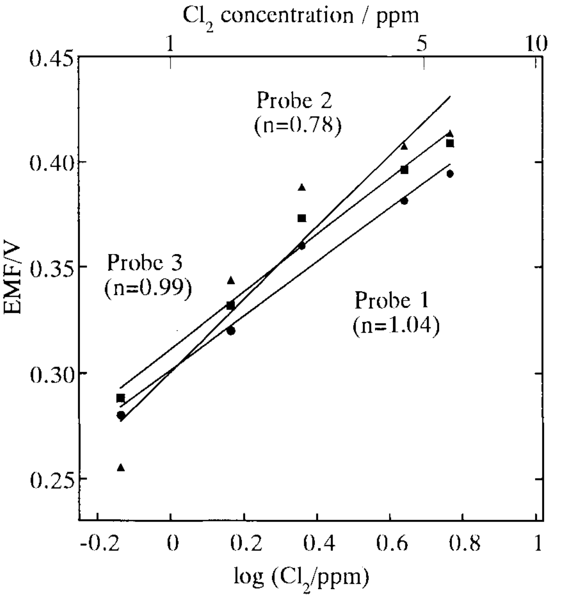

Figure 3. Relationship between EMF and Cl_2 gas concentration at 400 °C for the sensor probes prepared using a NASICON-glass composite electrolyte and a RuO_2-NaCl (1:1) measuring electrode.
Probe 1 (●), Probe 2 (▲), Probe 3 (■)

The relationship between the 90% response time (R) and the reciprocal flow rate (1/F) is plotted in Figure 4. This R-1/F relation is very useful to discuss the reaction on the measuring electrode.[6] When the response time is limited only by the gas exchange in the test chamber, the observed 90 % response time is proportional to the reciprocal flow rate and is negligible for 1/F=0 (i.e., F=∞). However, the 90 % response time hardly depended on the flow rate, and the extrapolated R values for 1/F=0 deviated from zero. This result and the low measured *n* value suggest us that the reaction (1) on the measuring electrode was not the rate-determining step and a side-reaction occurred at the measuring electrode. The 90 % response time for high concentrations was about 2 min, and increased with a decrease in the Cl_2 gas concentration. These observations allowed us to consider the same reaction as the total reaction (3) as the side reaction at the measuring electrode. The Gibbs free energy for the reaction is -371 kJ/mol at 400 °C.[7] This side reaction at the measuring electrode would reduce the rate of reaction (1), affecting the electron number *n* and the response time.

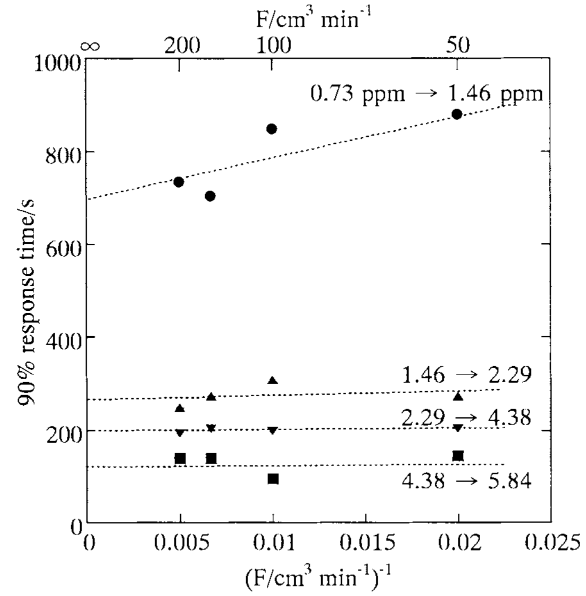

Figure 4. The relationship between the 90 % response time and the reciprocal flow rate at 400 °C. The concentration changes are indicated in ppm.

The O_2 and CO_2 gas contents are variable in most of the practical applications for Cl_2 gas sensors. Therefore, the tests were performed changing O_2 (0% ⇔ 20%) and CO_2 (1~2 ppm ⇔ 10000 ppm) gas concentrations, the sensor EMF response, however, was hardly influenced by the O_2 and CO_2 gas concentration changes.

In conclusion, good EMF responses were obtained for a sensor prepared using a composite Na^+ conductor and a RuO_2+NaCl measuring electrode even for sub-ppm level of Cl_2 gas concentration (below 6 ppm). However, a side-reaction between Na_2O and Cl_2 gas occurs at the measuring electrode. Further work will be performed reduce the influence of the side-reaction, by using Na^+ conductors containing smaller amounts of Na for the Cl_2 gas sensor.

References and Notes

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