Cl_2 Gas Detection at Low Temperature Using the $0.97PbCl_2$-0.03KCl Solid Electrolyte Prepared by the Melting Method

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A Cl_2 gas sensor with a $0.97PbCl_2$-0.03KCl solid electrolyte and a Pb reference electrode was prepared by a melting method using an evacuated closed tube. The electromotive force (EMF) measured at 573 K agreed with the calculated value for Cl_2 gas concentrations from 10 ppm to 1000 ppm. The response time was long when the operating temperature is lower than 473 K.

Chlorine exhaust gas has become a serious problem with regard to air pollution and acid rain in recent years. Several gas sensors using solid electrolyte have been investigated in order to determine the concentration of the Cl_2 exhaust gas.[1-6] The Cl^- ionic conductors of the $PbCl_2$-KCl system,[1,2] the $SrCl_2$-KCl system,[3] and the $BaCl_2$-KCl system[4-6] were used as the solid electrolyte for the gas sensor. For detection at low temperature, the $PbCl_2$-KCl electrolyte is the most suitable material because of its high conductivity[7] and high stability in humid gas. Niizeki et al. first attempted Cl_2 gas detection at room temperature with a gas sensor using the $PbCl_2$-KCl solid electrolyte.[1,2] However, the electromotive forces (EMF) values at room temperature did not agree with the theoretical values and the EMF response was very slow at low temperature. In addition, the electrolyte for the sensor probe was prepared by pressing the electrolyte powder. This method does not allows the highly dense electrolyte to be obtained by sintering. Furthermore, the gas sensor using electrolyte prepared by this method has several problems including fragility of the sensor probe and difficulty of sensor preparation. We have reported a Cl_2 gas sensor with a $BaCl_2$-KCl solid electrolyte prepared using a melting method.[4-6] All the problems associated with the pressing method were overcome by using the melting method preparation. However, the gas sensor using the $BaCl_2$-based electrolyte is not able to operate at low temperature (<523 K) because of the low electrolyte conductivity.

In this paper, we investigate the EMF response of a Cl_2 gas sensor using a $0.97PbCl_2$-0.03KCl solid electrolyte prepared by the melting method in order to clarify the influence of the operating temperature.

The $0.97PbCl_2$-0.03KCl solid electrolyte with a Pb reference electrode was utilized for the sensor probe. Pb powder (99.9%, ca. 5 g) and a stoichiometric mixture (ca. 4 g) of $PbCl_2$ (99.9%) and KCl (>99.5%) were placed in a quartz tube. The sample was dried at 473 K for 30 min and then evacuated and sealed. The material in the evacuated closed quartz tube was melted at 873 K for 30 min. The Pb metal (liquid: 11.3 g/cm^3, m.p.: 600 K) and the formed solid solution of $0.97PbCl_2$-0.03KCl (ca. 5.9 g/cm^3) naturally separated by the difference in their specific gravity. The tube containing the electrolyte was cut using a diamond wheel. The Pb reference electrode was connected to a Ag terminal wire. The sensor probe was assembled using an inorganic bonding agent. RuO_2 electrode powder (Katayama Chemical, 99.9%) was painted on the surface of the electrolyte and then heated at 573 K for 1 h. Figure 1 shows the sensor

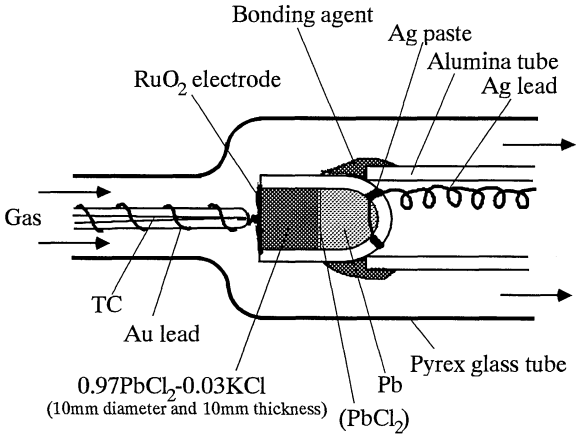

Figure 1. Apparatus for the EMF measurements.

apparatus used for the EMF measurements. The sensor probe was fixed in a Pyrex glass tube and an Au lead with a thermocouple was attached to the measuring electrode. A standard Cl_2 gas (840 ppm or 105 ppm in N_2) was diluted with air. The gas flow rate, F (ml/min), is the value at room temperature, and it was uncorrected for the operating temperature of the sensor probe. The EMF measurement was made using an Electrometer HE-106 (internal resistance $>10^{14}$ Ω) from Hokuto Denko Company.

The following cells were employed:

Cl_2, RuO_2 / $0.97PbCl_2$-0.03KCl / ($PbCl_2$), Pb

The EMF between the measuring and reference electrodes obeys the Nernst equation. For the reference electrode, the following equilibrium exists.

$$Pb + Cl_2 \rightleftharpoons PbCl_2 \qquad (1)$$

When the activities of $\mathbf{a}_{Pb}$ and $\mathbf{a}_{PbCl2}$ are equal to 1, the reference Cl_2 pressure is fixed by the formation of $PbCl_2$. The theoretical EMF value was calculated from:

$$EMF = (-\Delta G^0/2F) + (RT/2F) \ln (P_{Cl2}) \qquad (2)$$

where ΔG^0, R, T, and P_{Cl2} are the standard Gibbs energy of formation, the gas constant, absolute temperature, and Cl_2 partial pressure at the measuring electrode, respectively.[8,9]

In the case of the Cl_2 gas sensor using a $BaCl_2$-based solid electrolyte, we could not detect any EMF responses below 523 K.[4-6] In this $PbCl_2$-based sensor, a stable EMF was observed even at room temperature. Figure 2 presents the relationship between the EMF at 373~573 K and the Cl_2 partial pressure for a sensor probe prepared by the melting method using an evacuated closed tube. The EMF at 573 K showed good agreement with

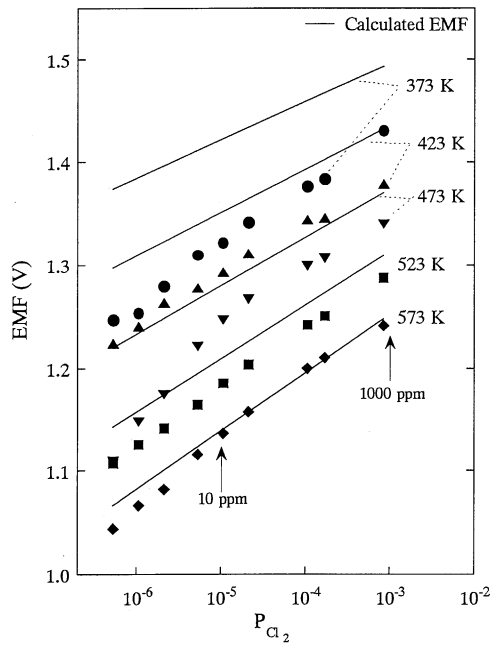

Figure 2. Relationship between the EMF at 373～573 K and Cl_2 concentration for the probe using $0.97PbCl_2$-0.03KCl prepared by the melting method using an evacuated closed tube at 373 K (●), 423 K (▲), 473 K (▼), 523 K (■), and 573 K (◆).

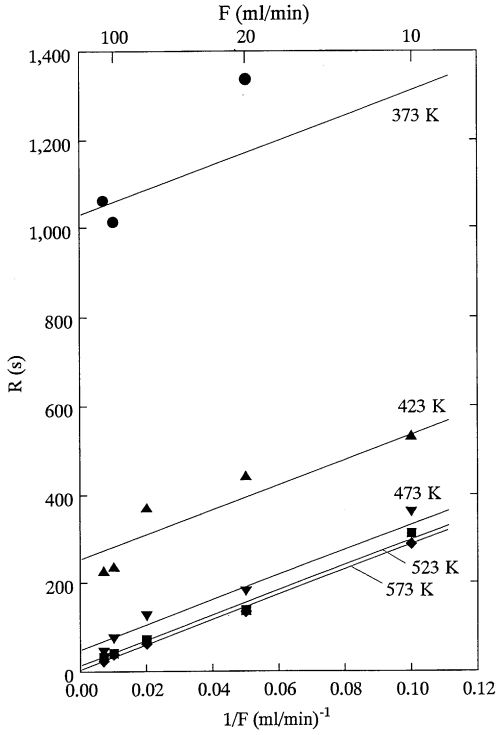

Figure 3. Relationship between the 90% response time and the reciprocal of the flow quantity (cm^3/min) when the Cl_2 concentration is changed from 20 ppm to 100 ppm at 373 K (●), 423 K (▲), 473 K (▼), 523 K (■), and 573 K (◆).

the calculated values for Cl_2 gas concentrations from 10 ppm to 1000 ppm. However, the EMFs at lower temperatures did not agree with the theoretical value. Figure 3 shows the relationship between the 90% response time and the reciprocal value of the flow rate (1/F). This R-1/F relation is very useful to discuss the reaction on the measuring electrode, because the gas exchange time is negligible for 1/F=0 (i.e., F=∞).[6] The response time increases with a decrease in the gas flow rate, and is almost proportional to 1/F. If the response time depends on only the gas exchange time, the extrapolated response time of 1/F=0 should approach zero. However, the extrapolated response time for 1/F=0 is not zero at low temperature, it remains a positive value. Figure 4 shows the response time at 1/F=0 for both probes at 373~573 K. Although the response time is very close to zero above 473 K, it significantly increases with decreasing temperature. This increase is attributed to the low catalytic activity of the RuO_2 electrode at low temperature. The rate-determining step at low temperature is the Cl_2 ionization step on the RuO_2 measuring electrode.

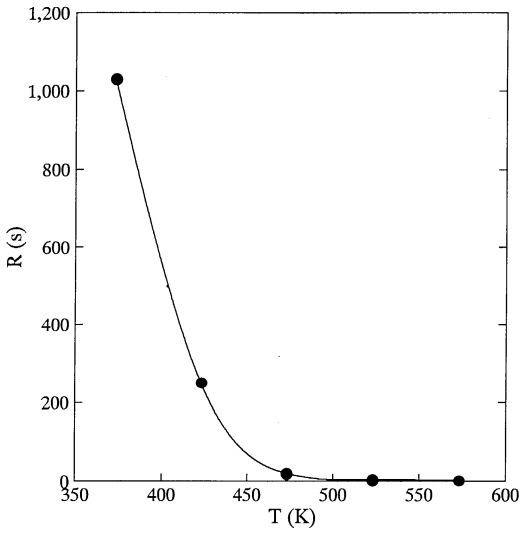

Figure 4. The temperature dependence of the 90% response time at 1/F=0.

From this data, we determined the most suitable temperature for Cl_2 detection as 573 K because of its EMF agreement with the theoretical value and rapid response.

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