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DETECTION OF COMBUSTIBLE GASES WITH STABILIZED ZIRCONIA SENSOR

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Calcia stabilized zirconia sensors can be used for detection of combustible gases contained in oxygen atmosphere. The sensitivity (e.m.f.) depends strongly on temperature and far exceeds the level expected from gas combustion at lower temperatures of 550∿600°C. It is strongly suggested that the high sensitivity is associated with the catalytic properties of the electrode metals used.

Calcia stabilized zirconia has successfully been used for oxygen sensors[1]. A galvanic cell is constructed between two oxygen atmospheres through the stabilized zirconia, a well known oxygen ion conductor[2)3)], and the e.m.f. generated gives the partial pressure of oxygen on one side with reference to that on the other side. In the present study, however, we examined the detection of combustible gases contained in oxygen atmosphere using such sensors, and found that combustible gases could be detected with unexpectedly high sensitivity.

The sensors used were prepared by fitting electrodes at the inside (reference electrode) and outside (detection electrode) of the closed end of the purchased zirconia Tamman tube (standard 8mmϕ×30cm). As the detection electrode, Pt or Pd foil (∿100μ thick) was fixed with Pt paste and as the reference electrode an wound Pt wire was pressed against the zirconia wall. This tube was set in a quartz tube and heated in an electric furnace. With pumping fresh air over the reference electrode, diluted combustible gases were manipulated to flow over the detection electrode, while the e.m.f. was continuously monitored.

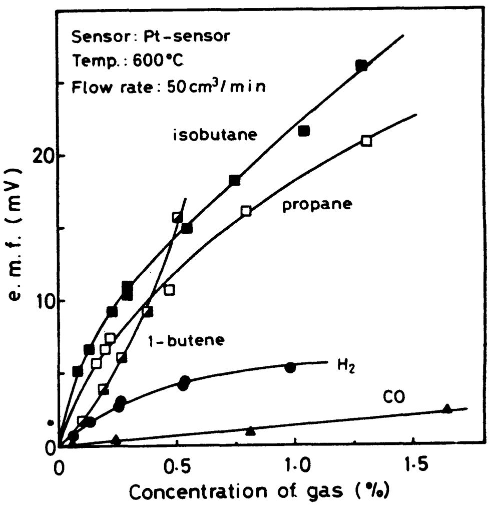

Fig. 1 The dependence of electromotive force on gas concentration

Above ca 550°C, the quick and reversible responce of the e.m.f. was observed on introduction of the combustible gas flow and subsequent change to air flow. Assuming a decrease in oxygen partial pressure on the detection electrode due to total oxidation of co-existing combustible gases, the e.m.f. can be easily estimated using Nernst equation. Interestingly, however, the observed e.m.

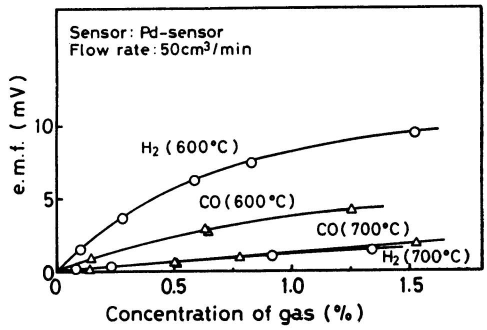

Fig. 2 The dependence of electromotive force on gas concentration

f. was usually much larger than expected. Owing to such unusually large e.m.f., the concentrations of combustible gases can be measured rather sensitively at adequate temperatures. A few examples of observed e.m.f. are shown in relation to combustible gas concentration in Figs. 1 (Pt foil electrode) and 2 (Pd foil electrode). Measurements were carried out for the following gases; 1-butene, isobutane, propane, H_2, and CO. The observed e.m.f. is strongly dependent upon temperature, the kind of combustible gas, and the kind of electrode. Fig. 3 shows the ratio of the observed e.m.f. to the calculated e.m.f. mentioned above as a function of temperature for various gases (0.5%). Generally speaking, the ratio approaches unity with increasing temperature, while at too low temperatures the ratio became scattered probably due to an increasing difficulty of oxygen ion transport in zirconia. From these results, the temperature range preferable for combustible gas detection appears to be 550∿600°C.

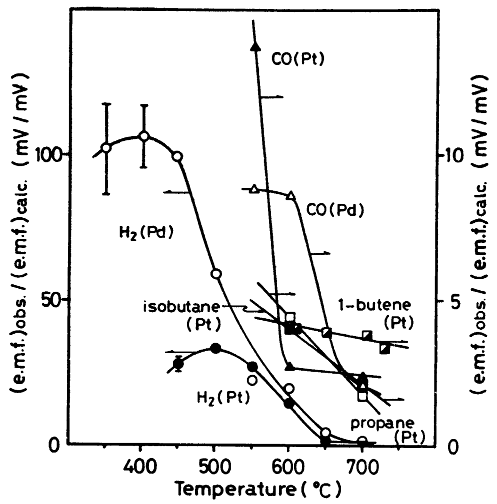

Fig.3 The dependence of responce on temperature
Gas concentration: 0.5%

It was suspected at the first stages of this study that the unexpectedly large e.m.f. was associated with hydrogen permeation through the noble metal electrodes. However, this was denied from the fact that a similar phenomenon was also observed in the case of CO detection. The phenomenon is probably associated with the catalytic activity of the electrode metals for the complete oxidation of gases[4]. It is considered that combustible gases are selectively adsorbed on the electrode and oxidized consuming oxygen gas nearby. As a result, the partial pressure of oxygen decreases locally at the zirconia-electrode interface to a level far below that expected in the homogeneous gas phase oxidation. Such a phenomenon has not been reported so far. It is also inferred that care must be paid when zirconia sensors are used for monitoring oxygen concentration in the presence of combustible gases as in automobile exhaughsts[1].

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