Efficiency of Noble Metal Electrodes for Zirconia Oxygen Sensors in Detecting Oxygen at Lower Temperatures

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Synopsis. Metal Au, Ag, or Pt was deposited as electrode on the closed end of a stabilized electrolyte tube in the ZrO_2 oxygen sensor, and emf of the cell, $O_2|m|ZrO_2$–$Y_2O_3|m|O_2'$ (m=Au, Ag, Pt) with $P_{O_2}=8.8$ and $P_{O_2'}=159$ Torr (1 Torr=133.322 Pa), was measured as a function of temperature between 150 and 950 °C. For cells with Ag electrodes, a good agreement is found between theoretical and measured emf's at lower temperatures (*ca.* 340 °C).

Solid oxide electrolytes are in use for construction of oxygen sensors, high temperature fuel cells, and oxygen pumps.[1–3] However, for their practical use, for example, electrodes in the system of O_2|stabilized zirconia|O_2' play an important part. In this connection, a number of studies have been made of the use of Pt electrodes on stabilized electrolyte,[4] but no reports have been published of the other noble metal electrodes. The object of the present work is to investigate the efficiency of noble metal electrodes for stabilized zirconia oxygen sensors in detecting oxygen at lower temperatures.

Experimental

The solid electrolytes used were impervious ZrO_2–Y_2O_3 (8 mol%), ZrO_2–CaO(11 mol%), and ZrO_2–MgO(15 mol%) tubes closed at one end. The electrolyte tube had an i.d. of 11 mm, an o.d. of 15 mm, and a length of 300 mm. Each noble metal was first deposited on both the inside and outside surfaces near the closed end of the electrolyte tube. One Pt electrode was prepared by applying a nonfluxed platinum paste consisting of submicron platinum powder suspended in a 5:1 mixture of ethanol and surface active agent. This was heated to 800 °C for 30 min in air and then 1200 °C for 1 h in an atmosphere of hydrogen. One Au electrode was prepared by brushing a nonfluxed gold paste onto the surface of the electrolyte, and then firing at 600 °C for 2 h in an atmosphere of hydrogen. Three Ag electrodes were prepared in three ways: (i) Silver paste was applied on the surface of the electrolyte and fired at 600 °C for 2 h in a stream of hydrogen. (ii) When a formaldehyde solution was added dropwise to a 20% silver nitrate solution to which an excess ammonia solution had been added, silver was deposited on the faces of stabilized zirconia. This procedure was repeated twice or three times. The faces were washed with distilled water, dried at 100 °C and then heated at 600 °C for 2 h in a stream of hydrogen. (iii) A thin film on the surface of electrolyte was prepared by evaporation of silver metal and then heated at 600 °C for 2 h in an atmosphere of hydrogen. As illustrated in Fig. 1, the electrolyte tube was placed inside a quartz tube closed at one end. The electrolyte tube and the quartz tube were connected to the brass heads and the assembly was tightly closed by o-ring. Each of the inner and outer electrodes was linked by a Pt wire to the output terminal. A Pt *vs.* Pt/13% Rh thermocouple was used to measure temperatures. The outside of the electrolyte tube was kept in 159 Torr O_2 and the inside was allowed to contain 8.8 Torr O_2. The effectiveness of these noble metal electrodes was determined by measuring the emf of the cell $O_2|m|Zr|m|O_2'$, where m is the metal electrode and Zr is the electrolyte as follows:

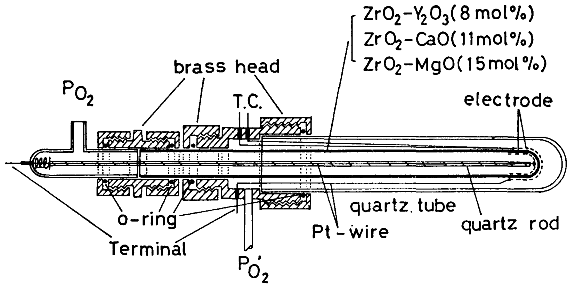

Fig. 1. Experimental cell assembly for evaluating the performance of the oxygen sensor.

Cell number	Electrolyte (Zr)	Electrode (m)
1	ZrO_2-Y_2O_3	Pt
2	ZrO_2-Y_2O_3	Au
3	ZrO_2-Y_2O_3	Ag
4	ZrO_2-CaO	Ag
5	ZrO_2-MgO	Ag

In addition, the emf vs. relative oxygen-pressure ratio was determined by stepwise change of the inside oxygen partial pressure from 130 to 1 Torr, with the outside pressure kept 159 Torr. The emf was measured with a Takeda Riken electrometer. Measurements were carried out at 400—950 °C (Pt electrode) and 150—950 °C (Ag and Au electrodes).

Results and Discussion

In order to compare the abilities of the noble metal electrodes, each electrode prepared by applying the nonfluxed metal paste was tested, typical results being shown in Fig. 2. The solid line represents the theoretical emf as obtained from

$$E = \bar{t}_i \frac{RT}{4F} \ln \frac{P_{O_2'}}{P_{O_2}}, \tag{1}$$

where $\bar{t}_i=1$. All the noble metal electrodes, except the Au electrode (cell 2), were reversible in the measured temperature range, but the Ag electrode was deteriorated at temperatures over *ca.* 960 °C. With the cell $m|ZrO_2$–$Y_2O_3|m$, measurement of emf for the Ag electrode (cell 3) was possible from about 250 °C and a good agreement began around 340 °C to be found between the theoretical and measured emf's. Since the activity is in parallel with the temperature (T_g) at which the agreement between the theoretical and measured emf's begins, the sequence of activities for the noble metal electrodes is Ag>Au>Pt. Further, the emf-temperature curves for the other Ag electrodes

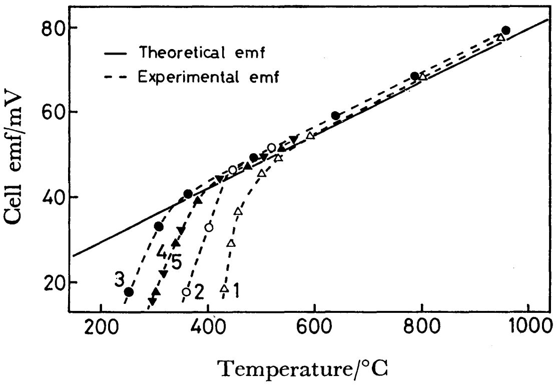

Fig. 2. Theoretical and experimental emf *vs.* temperature for the cell, where $P_{O_2}=8.8$ Torr and $P_{O_2'}=159$ Torr. The figures are cell number (see text).

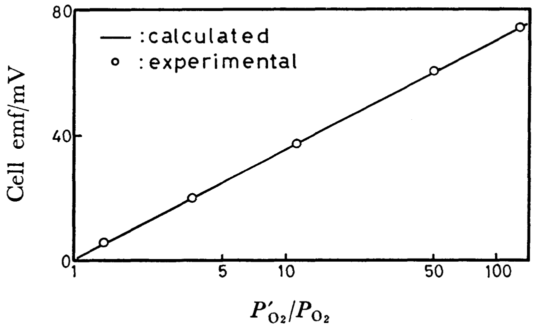

Fig. 3. Dependence of emf on $P_{O_2}/P_{O_2'}$ for cell 4, $P_{O_2}|Ag|ZrO_2$–$Y_2O_3|Ag|P_{O_2'}$, where $P_{O_2'}=159$ Torr.

are similar to that for the Ag paste electrode, whereas for the other cells using Ag electrodes both cells 4 and 5 have T_g values slightly higher than that of cell 3. Thus it is concluded that electrodes greatly affect the detection of oxygen at lower temperatures and that the cells with Ag electrodes are better than those with the other electrodes.

In order to test the dependence of emf on $P_{O_2'}/P_{O_2}$, the emf of cell 3 was measured at 350 °C with P_{O_2} changed from 130 to 1 Torr. As shown in Fig. 3, the emf is proportional to $\ln P_{O_2'}/P_{O_2}$ and the slope is in good agreement with that calculated by using Eq. 1. Consequently, the cells with Ag electrodes may have the capability of detecting oxygen at lower temperatures, as described above.

Further, it is noted that for the cells with Ag or Pt (except Au) electrodes, T_g is close to the decomposition temperature, 300 or 560 °C, of the corresponding metal oxide Ag_2O or PtO, respectively.[5] In a potentiostatic experiment, Rickert and Steiner[6] found that for a cell Fe(FeO)|electrolyte|Ag,O_2 the oxygen moves from the silver electrode through the electrolyte to the opposite electrode, no product in the silver electrode being identified, whereas Belford and Alcock,[7] on the basis of findings obtained by using the galvanostatic technique, reported that, with respect to the diffusivity of oxygen through liquid tin, some evidence for limiting potential had been obtained at oxygen activities corresponding to those expected for unstable solid SnO. Thus it is concluded that cleavage of the metal-oxygen bond, which has been formed between the metal atom and the oxygen dissolved in the electrode, is an important process for the detection of oxygen at lower temperatures. Further physicochemical evidence shold be collected to support this result.

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