Preparation and Characterization of a Zirconia Oxygen Sensor with an Internal Reference for Low-Temperature Operation

Hiroyuki Kaneko,* Hiroaki Sato, and Hitoshi Taimatsu
Department of Materials Science and Engineering, Faculty of Engineering and Resource Science, Akita University, Akita 010-8502

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A miniature zirconia oxygen sensor with a Ag-based electrode as a measuring electrode and with a Cu/Cu_2O or Pd/PdO electrode as an internal reference electrode is workable at low temperatures even near 550 K in a wide range of oxygen pressures.

Potentiometric zirconia oxygen sensors are widely used to detect oxygen pressures in gases at high temperatures.[1] At present, nevertheless, they do not work well at temperatures below 700 K because electrolyte and electrode resistances, especially the latter, become remarkably high. In order to solve this problem, both the selection of electrode and the design of the device need to be taken into consideration. It is well known that Ag electrodes are superior to conventional Pt electrodes at low temperatures;[2, 3] previously, the authors[4] reported that a Ag electrode operated satisfactorily at about 600 K as an oxygen electrode. Therefore, improved Ag-based electrodes are suitable candidates for use at low temperatures. As for the design of the device, several types of miniature sensors have been proposed. Fouletier *et al.*[5] constructed a device incorporating an internal reference by filling and sealing a closed-end miniature zirconia tube with Pd and PdO powders; it measured oxygen partial pressure with a superior performance at temperatures down to 723 K. This suggests that devices with an internal reference can respond well even at low temperatures. In this study, the challenge was to make a new type of a miniature device, with a metal/metal oxide internal reference, which would operate at temperatures below 600 K.

Figure 1 shows a schematic diagram of the device prepared in this study. A disc of diameter 10 mm and thickness 2 mm of ZrO_2-8 mol% Y_2O_3 (YSZ) electrolyte (Tosoh) was drilled to make a cavity of diameter 6 mm and depth 1 mm. The cavity was filled with selected metal powders to act as an internal reference electrode. An internal Pt lead wire was insulated with a glass having a high melting point and located through a slot on the side of the disk. The disk was covered by another thin YSZ disc of diameter 10 mm and thickness 0.3 mm with the same dopant content as the first and then sealed using a glass frit with a low melting point, firing at 823 K for 30 min in Ar gas. Such a low-temperature short firing was effective for preventing the particles of the metal powders from coarsening. As an outer electrode a Ag-based powder was smeared onto the outer side of the thin disk, covered with Pt gauze electrode and then co-fired at 703 K for 1 h in Ar gas.

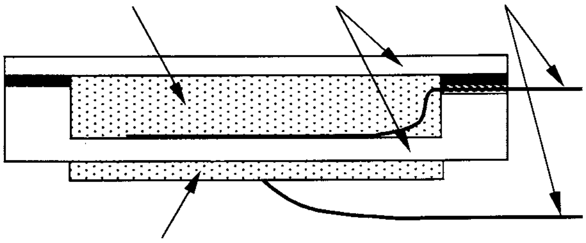

Figure 1. Schematic diagram of a miniature oxygen sennsor with an internal reference electrode.

As internal reference, Cu and Pd were chosen in this study. Cu and Pd are readily oxidized to Cu_2O and PdO by residual air in the cavity. Therefore, without intentional addition of Cu_2O or PdO, equilibrium oxygen partial pressure of a Cu-Cu_2O or Pd-PdO couple was maintained at any given temperature. The equilibrium oxygen partial pressures of these couples are higher than most other metal/metal oxide combinations, as clearly shown in the Ellingham diagram. A metal/metal oxide internal reference with a high equilibrium oxygen pressure has a high buffer capacity of oxygen and, as a result, the equilibrium oxygen pressure is liable to be maintained, irrespective of leakage of oxygen from the surroundings.

The outer electrode, responsive to oxygen in an ambient gas, is required to work at temperatures as low as possible. In this study, a Ag paste mixed with a $La_{0.85}Sr_{0.15}MnO_3$ powder was used as an improved Ag electrode. $La_{0.85}Sr_{0.15}MnO_3$ is one of the conductive ceramics, which is used as a cathode material for solid oxide fuel cells using zirconia electrolytes due to its high electrochemical catalytic activity.[6, 7] A preliminary experiment by complex impedance spectroscopy showed that electrode resistance for a $La_{0.85}Sr_{0.15}MnO_3$-dispersed Ag electrode was lower than that for an YSZ-dispersed Ag electrode. In this work a $La_{0.85}Sr_{0.15}MnO_3$ powder was added to prevent grain growth of Ag which resulted in increase in electrode resistance. In addition, it was found to be critical that operating temperatures were maintained as low as possible, in order to reduce grain growth of electrode.

The temperature dependence of the EMF of the device measured in Ar-0.01% O_2 as a test gas is shown in Figure 2. From the highest temperature investigated to lower temperatures, the EMF change obeyed the Nernst equation, which was calculated and extrapolated from literature values[8, 9] for the equilibrium oxygen partial pressure of the internal reference at high temperatures. This device worked even down to 563 K for Cu-Cu_2O and to 553 K for

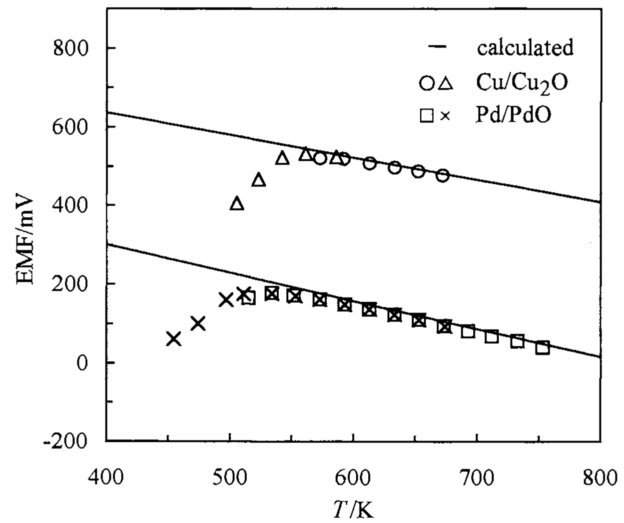

Figure 2. Dependence of EMF on temperature for sensors with Cu/Cu_2O and Pd/PdO reference electrodes in 10^{-4} atm.

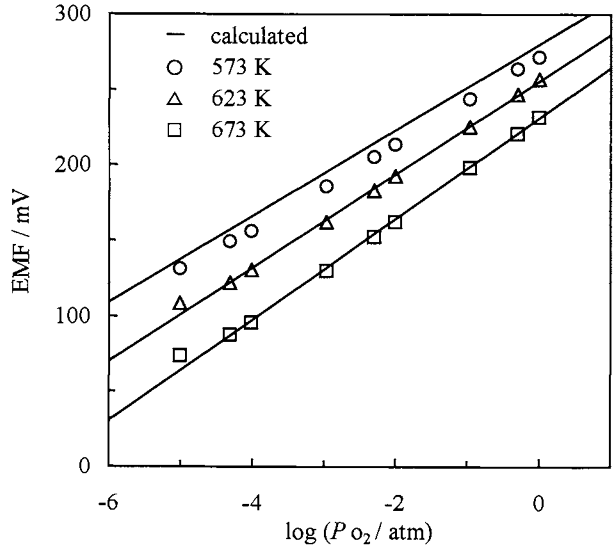

Figure 4. Dependence of EMF on oxygen pressure for a Pd/PdO reference electrode.

Pd-PdO. When the temperature was lowered further, the EMF deviated from that predicted by the Nernst equation and it took more than 1 h to reach stable EMF values. Figures 3 and 4 show the oxygen pressure dependences of the EMF measured at 573, 623 and 673 K for a Pd/PdO and a Cu/Cu_2O reference electrode, respectively. The data obeyed the Nernst equation in a wide range of oxygen pressure from 10^{-5} to 1 atm. These results show that this device works well as an oxygen sensor at temperatures down to about 560 K in a wide range of oxygen pressures. The lower temperature limits of equilibrium oxygen partial pressure determined by the EMF method reported in the literature are 700 K for $Cu-Cu_2O$[7] and 659 K for Pd-PdO.[10] This sensor well responded at temperatures about 100 K lower than those reported in the literature. Response characteristics are improved by making a miniature device with an internal reference. As internal references, $Cu-Cu_2O$ and Pd-PdO are effective. By using a Ag-based electrode with a relatively high equilibrium oxygen partial pressure, the electrode characteristic is improved at low temperatures. This device is very useful for detecting oxygen partial pressure, especially at temperatures below 700 K. This means that if another metal-metal oxide is used as the internal reference, equilibrium oxygen partial pressure of the metal-metal oxide can be measured at low temperatures. As shown in this study, a disc-type miniature device also is a powerful tool for measuring equilibrium oxygen pressure for metal-metal oxide systems at low temperatures.

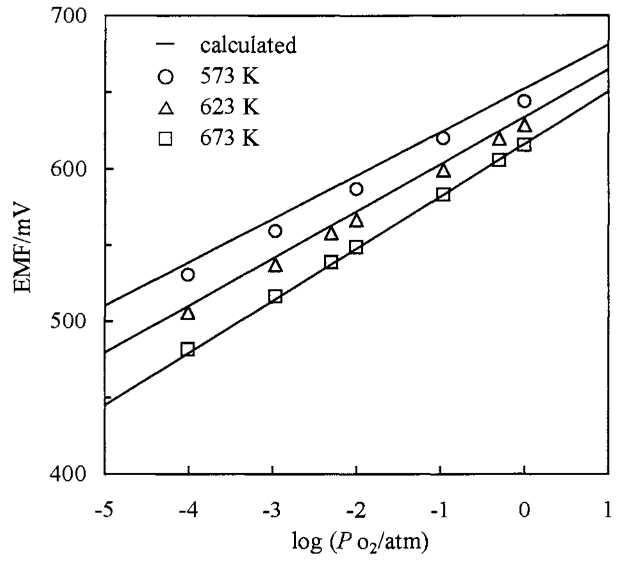

Figure 3. Dependence of EMF on oxygen pressure for a Cu/Cu_2O reference electrode.

References and Notes

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