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TRANSIENT BEHAVIOR OF THE ELECTROMOTIVE FORCE OF AN OXYGEN SENSOR INDUCED BY THE TEMPERATURE CHANGE

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When the operating temperature of an oxygen sensor with a zirconia-based electrolyte was changed rapidly during the measurement of the oxygen partial pressure in argon, an abnormal electromotive force was transiently generated. This phenomenon is attributed to the transient variation of oxygen concentrations at the electrolyte/electrode interfaces.

An oxygen sensor, which consists of a pair of gas compartments with electrodes in contact with both sides of a zirconia-based electrolyte, is widely used to determine the oxygen partial pressure in gas mixtures.[1-3] The electromotive force (EMF) of the sensor is given by the Nernst equation, $E=(RT/4F)\ln(P''/P')$, where P'' and P' are oxygen partial pressures in the respective gas compartments. On examining the response of the EMF of the sensor to the operating temperature, the authors found that an abnormal EMF change, which was not due to a delay of the temperature response, was transiently produced by the rapid change of the temperature when the oxygen partial pressure was being measured in argon. In this communication, the generation of the abnormal EMF and its characteristics are reported.

A measuring system was a gas-tight system consisting of a gas-introducing device made of Pyrex glass tube and an oxygen sensor with $(ZrO_2)_{0.89}(CaO)_{0.11}$ solid electrolyte tube in a fused quartz tube, as described elsewhere.[4] Air ($P(O_2)=0.21$ atm) was used as a reference gas. Commercial argon was used as a feedgas. Both the air and the argon were passed at a constant flow rate of 3.33 $cm^3\ s^{-1}$.

The transient EMF changes of the oxygen sensor induced by heating or cooling the cell were investigated. Figure 1 shows typical results obtained in the cell

$Pt \mid Ar\ (P(O_2) \approx 4 \times 10^{-7}\ atm) \mid (ZrO_2)_{0.89}(CaO)_{0.11} \mid air \mid Pt$, in which the air and the argon were passed inside and outside the electrolyte tube, respectively. As the temperature was elevated at a constant rate from a steady-state value, the EMF first decreased, the direction of the EMF change being opposite to that expected from the Nernst equation, and then began to increase (see Fig. 1-(a)). As the temperature was lowered, the response was reversed (see Fig. 1-(b)). Further, the deviation of the measured EMF from the Nernstian value increased with increasing the rate of the temperature change and with decreasing the oxygen partial pressure in argon.

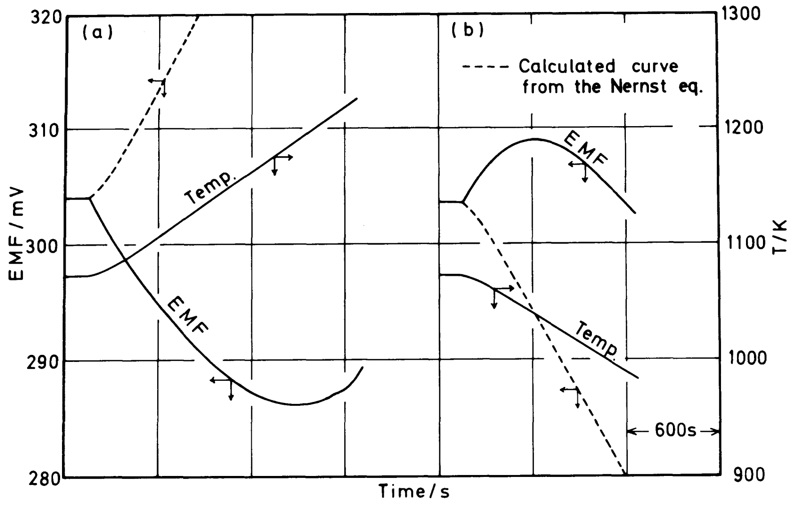

Fig. 1. Transient behavior of the EMF of the oxygen sensor induced by heating (a) and cooling (b) the cell from 1073 K. Air and argon were passed inside and outside the electrolyte tube, respectively.
Cell:
$Pt \mid Ar \mid (ZrO_2)_{0.89}(CaO)_{0.11} \mid air \mid Pt$

These phenomena might be attributed to the thermoelectric effect, because the cell assembly was heated externally by an electric furnace and there was a transient temperature difference between the outer and inner sides of the electrolyte tube when the temperature was changed. In order to investigate the possible contribution of the thermoelectric force, an experiment was carried out with the cell $Pt \mid air \mid (ZrO_2)_{0.89}(CaO)_{0.11} \mid Ar\ (P(O_2) \approx 2 \times 10^{-6}\ atm) \mid Pt$, in which the argon and the air were passed inside and outside the electrolyte tube, respectively. The results are shown in Fig. 2. If the transient abnormal EMF were thermoelectric, the direction of the deviation of the EMF would be decided by the direction of the temperature gradient, independently of whether the air or the argon is passed outside or inside. In fact, however, the direction of the deviation of the EMF on heating or cooling the cell was reversed on interchanging the gases. Therefore, the generation of the transient abnormal EMF cannot be explained by the formation of the thermoelectric cell.

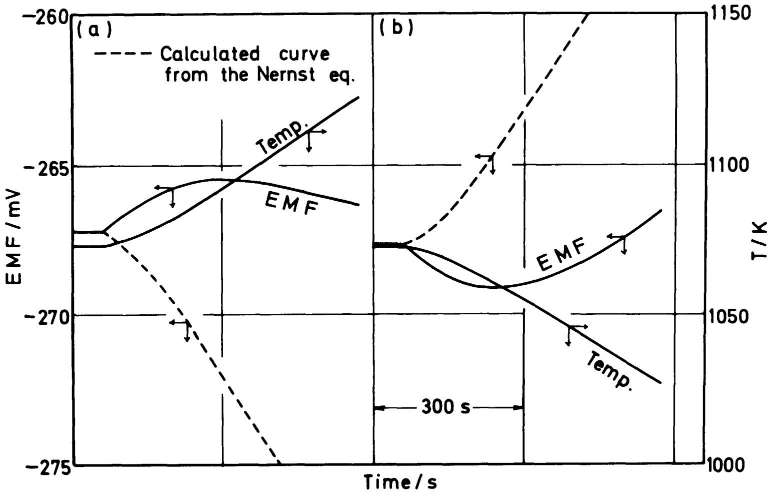

Fig. 2. Transient behavior of the EMF of the oxygen sensor induced by heating (a) and cooling (b) the cell from 1073 K. Argon and air were passed inside and outside the electrolyte tube, respectively.
Cell:
Pt|air|$(ZrO_2)_{0.89}(CaO)_{0.11}$|Ar|Pt

The effect of cyclic variation of the operating temperature on the EMF of the oxygen sensor is shown in Fig. 3. The EMF responded rapidly to the temperature variation, but in the opposite direction to that expected from the Nernst equation. The amplitude of the EMF oscillation increased with increasing the frequency of the temperature variation. Therefore, in order to obtain the steady EMF, the fluctuation in the operating temperature should be avoided as much as possible.

When a $CO-CO_2$ gas mixture ($P(CO)/P(CO_2)=1$) with high buffering capacity was used as a feedgas instead of argon with poor buffering capacity, the transient

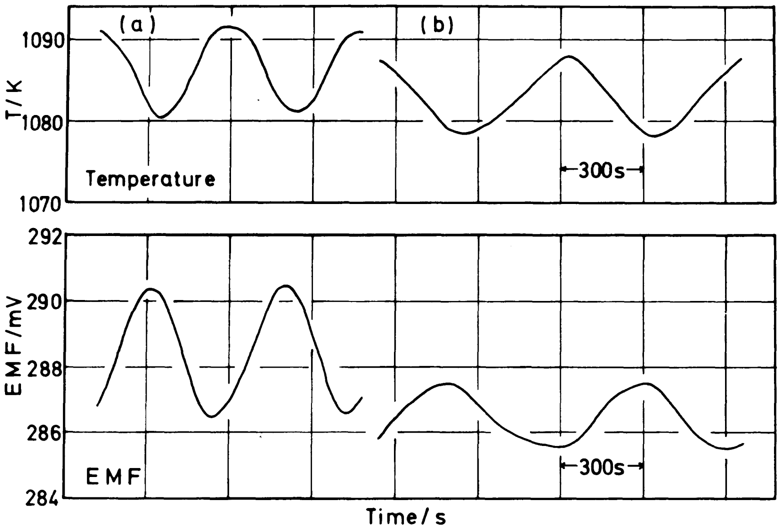

Fig. 3. Variation of the EMF induced by the cyclic variation of the temperature. Air and argon were passed inside and outside the electrolyte tube, respectively.
Cell:
Pt|Ar|$(ZrO_2)_{0.89}(CaO)_{0.11}$|air|Pt

abnormal EMF was scarcely detected. This shows that the abnormal EMF detected for argon is caused by the transient local variation of the oxygen concentration at the electrolyte/electrode interface induced by heating or cooling the cell.

These transient phenomena are phenomenologically interpreted as follows: (1) the increase in temperature results in temporary increase of oxygen at the lower oxygen partial pressure side; (2) the decrease in temperature results in temporary decrease of oxygen at the lower oxygen partial pressure side.

Possible mechanisms of the transient variation of the oxygen concentration at both sides of the electrolyte are as follows: (1) the leakage of oxygen from the higher oxygen partial pressure side to the lower oxygen partial pressure side through the electrolyte increases (decreases) with increasing (decreasing) temperature; (2) oxygen is released or desorbed (absorbed or adsorbed) at both sides of the electrolyte with increasing (decreasing) temperature, and then the oxygen concentration increases (decreases) in a greater extent at the lower oxygen partial pressure side, owing to the effect of the dilution with the bulk gas. As a result, the EMF decreases (increases) transiently by heating (cooling) the cell and tends to reach the steady value at a new temperature.

An analogous abnormal EMF by a sudden temperature change was reported in the Weston cell by Vinal and Howard.5) Similar behavior was observed in our preliminary experiment using the cell $Hg|Hg_2Cl_2|$sat. $KCl|AgCl|Ag$. These facts show that the phenomenon reported above may be expected to present itself quite generally in the electric cells.

References

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