CHEMISTRY LETTERS, pp. 1163-1166, 1990.

Mixed Oxide Capacitor of $BaTiO_3$-PbO as a New Type CO_2 Gas Sensor

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Mixed oxide capacitor of $BaTiO_3$-PbO is studied as the sensor for CO_2 detection. The oxide gave the large capacitance change on exposure to CO_2. The CO_2 sensing characteristics strongly depended on the operation temperature as well as the operation frequency. A linear relationship exists between the sensitivity and the concentration of CO_2 below 6%.

Detecting and controlling the concentration of CO_2 are increasingly required in various industrial processes as well as in environmental measurement. Although the infrared absorption method has been generally employed for CO_2 detection, various systems have recently been proposed as CO_2 sensor for the purpose of simplifying or miniaturizing the detection system.[1-4] Most of the reports on CO_2 sensor are based on the solid electrolyte-type,[5,6] whereas this type sensor has rather complex structure because reference electrode should be isolated from the environment. The change in capacitance of oxide capacitor is expected for detection of CO_2, since the dielectric constant of metal oxide generally differs from that of metal carbonates. Little is reported on the chemical sensors based on the capacitance change so far except for a humidity sensor. In the present study, mixed oxide of $BaTiO_3$-PbO was investigated as a new type CO_2 sensor based on the capacitance change.

Barium titanate was prepared by the calcination of an equimolar mixture of $BaCO_3$ and TiO_2 at 1473 K for 12 h. Thus obtained $BaTiO_3$ was mechanically mixed with commercialized PbO, and then pressed into disks (13 mm in diameter and 1 mm thick). After calcination at 773 K for 5 h, Ag paste was applied on the both faces of disks to make electrodes. After connecting Pt lead wire onto the electrodes with Ag paste, the element were dried at 373 K for 12 h. The capacitance of element was measured two probe method in a flow system. Sample gas was obtained by diluting the commercialized CO_2 gas with dry air. The capacitance of elements was measured with the LCR meter (Hioki, 3520). The sensitivity to CO_2 was

defined as the ratio of capacitance of element in a sample gas to that in air, C_{CO2}/C_{air}.

The changes in capacitance of $BaTiO_3$, PbO, and their equimolar mixture on exposure to 2% CO_2 were shown in Fig. 1. The introduction of 2% CO_2 does not change the capacitance of $BaTiO_3$, while slightly decreased that of PbO. On the other hand, the capacitance of equimolar mixture of PbO and $BaTiO_3$ decreased significantly on exposure to 2% CO_2. Since no reaction took place between PbO and $BaTiO_3$ during measurement, mixing PbO with $BaTiO_3$ seems to enlarge the capacitance change of PbO. It is expected that $BaTiO_3$ behaves as a semiconductor at the operation temperature, and the capacitance of the mixed oxide was greatly increased by mixing PbO with $BaTiO_3$. Mixed oxide capacitor of PbO-$BaTiO_3$, therefore, have some analogy to the barrier layer capacitor, and small change in capacitance of PbO was amplified by mixing with $BaTiO_3$. When PbO-$BaTiO_3$ was exposed to 2% CO_2, the capacitance of element rapidly decreased until 60 S and then gradually decreased (Fig. 1). This time dependence during exposure to CO_2 suggested the rapid carbonation of the surface and the following gradual carbonation of the bulk of PbO particles. The required time to attain eighty percent of the final capacitance change was 70 S, and its capacitance was restored to the original level after checking the CO_2 introduction. Although the mixed oxide capacitor required rather long time in response, time dependence of the capacitance of PbO-$BaTiO_3$ during transient exposure to CO_2 satisfys the demanded characteristics for CO_2 sensor.

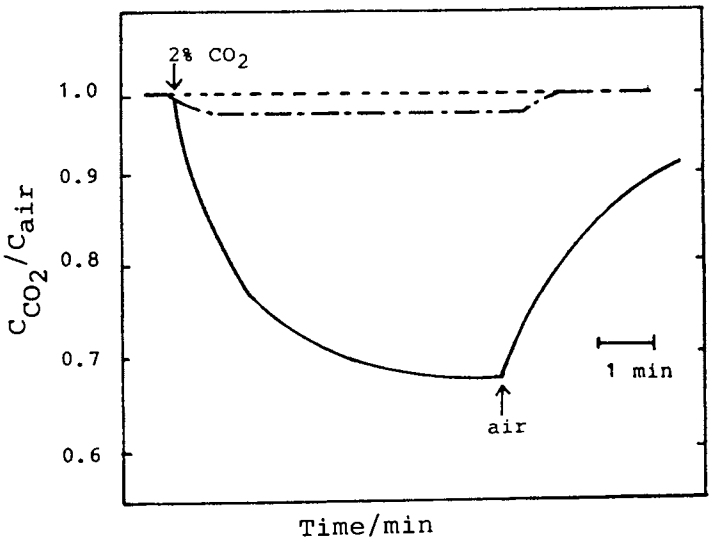

Fig. 1. Time dependence of the capacitance of PbO, $BaTiO_3$, and their equimolar mixture during transient exposure to 2% CO_2. (temperature; 773K, frequency; 50kHz)
—·—·— PbO ----- $BaTiO_3$ ——— PbO+$BaTiO_3$

The sensitivity of $BaTiO_3$-PbO is strongly depended on the applied ac frequency as shown in Fig. 2. With elevating the frequency, the sensitivity increased and attained a maximum at 50 kHz. The equivalent circuit of the sensor element can be expressed as an parallel circuit consisted of resistance and capacitance. The elevation of frequency enlarges the phase angle of impedance, so the capacitance component of impedance increased with elevation of frequency and attained the maximum at

the frequency of $(2\pi RC)^{-1}$, where R and C stand for the equivalent series resistance and capacitance of element, respectively.[7] It is expected that the frequency of $(2\pi RC)^{-1}$ on this element is near 50 kHz. Higher frequency is preferable for stabilizing the base line, but it decreases the sensitivity of the element. The optimum operation frequency of this capacitor, therefore, was determined to be 50 kHz.

The sensitivity of $PbO\text{-}BaTiO_3$ capacitor is plotted against the operation temperature in Fig. 3. The sensitivity to CO_2 increased with elevation of operation temperature and attained the maximum at 743 K. The first step in CO_2 detection on this sensor is believed to be the carbonation of PbO mixed with $BaTiO_3$. Elevation of operation temperature increased the rate of carbonation reaction resulting in the increased sensitivity to CO_2. On the other hand, operation temperature higher than decomposition temperature of $PbCO_3$ decreased the equilibrium yield of $PbCO_3$. The sensitivity to CO_2 on $PbO\text{-}BaTiO_3$, therefore, will have a maximum at 743 K, which is rather higher than the decomposition temperature of $PbCO_3$ (588 K).

The sensitivity of $PbO\text{-}BaTiO_3$ is shown in Fig. 4 as a function of CO_2 concentration. A linear relationship exists between the sensitivity and the concentration of CO_2 below 6 %. This charac-

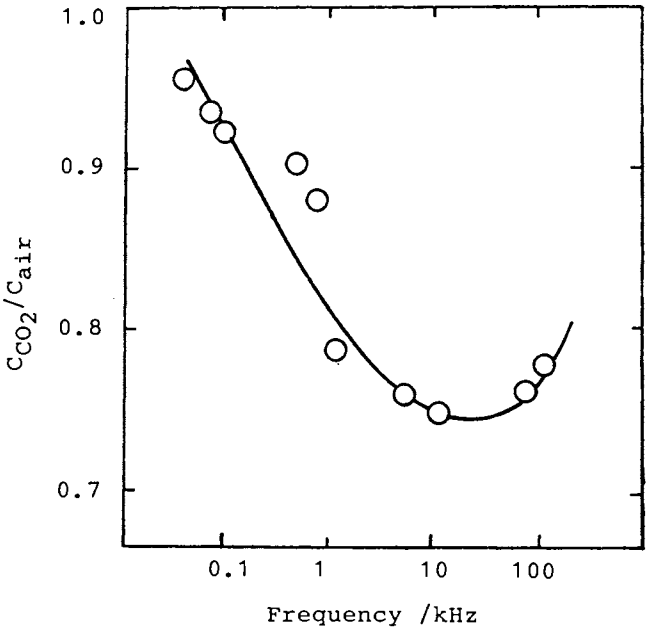

Fig. 2. AC frequency dependence of sensitivity of $PbO\text{-}BaTiO_3$ to 2% CO_2. (operation temperature; 820K)

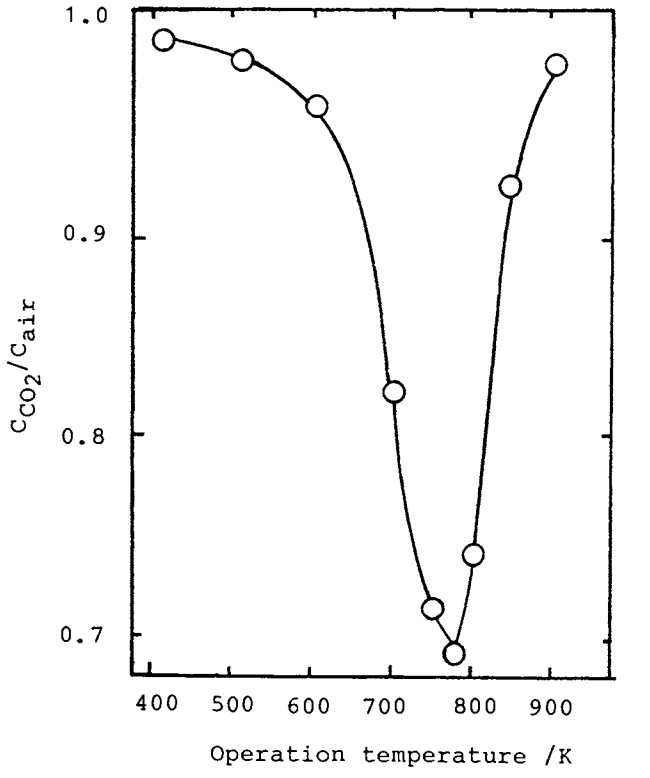

Fig. 3. Temperature dependence of sensitivity of $PbO\text{-}BaTiO_3$ to 2% CO_2. (Operation frequency; 50 kHz)

teristics enable us to evaluate the CO_2 concentration from the capacitance of the sensor element. But it is difficult to assume CO_2 concentration from the capacitance change of the element at CO_2 concentration higher than 6%. This may suggest that the most part of PbO in the element was carbonated to form $PbCO_3$ at CO_2 concentration above 6% CO_2. As a result, mixed oxide capacitor of PbO-$BaTiO_3$ can be used as CO_2 sensor in the CO_2 concentration range below 6%.

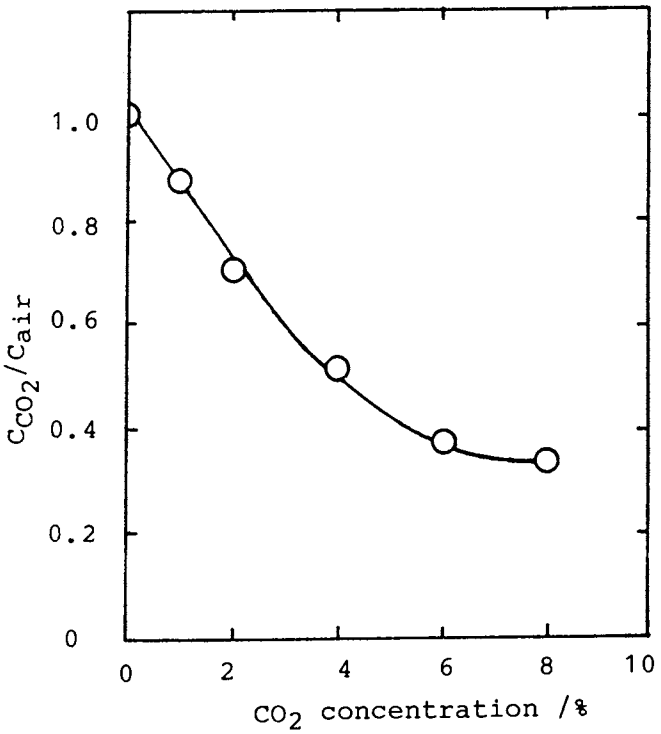

Fig. 4. Sensitivity of PbO-$BaTiO_3$ as a function of CO_2 concentration. (temperature; 743 K, frequency; 50 kHz)

It is expected that the interference of other gases for CO_2 detection is small on this oxide capacitor because the capacitance change of PbO-$BaTiO_3$ seems to be caused by the carbonation of PbO. It is also noted that the CO_2 sensing characteristics were dependent on the thickness of element, the area of electrode, and the operation temperature because these factors determine the capacitance of the element in air. Further investigation on CO_2 detection are now in progress.

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(Receved April 16, 1990)