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$BaCeO_3$-Based Protonic Conductor Sensitive to Ethanol

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A new type of potentiometric-type sensor for ethanol was constructed using proton conductive ceramic $BaCe_{0.95}Y_{0.05}O_{3-x}$ as a solid electrolyte. The sensing mechanism was discussed by measuring the reactivity of ethanol.

We have studied the detection of various gases using proton conductive ceramics as a sensor element. $SrCe_{0.95}Yb_{0.05}O_{3-x}$,[1] $BaCe_{0.9}Nd_{0.1}O_{3-x}$[2] and $CaZr_{0.9}In_{0.1}O_{3-x}$[3] are applicable to a potentiometric-type sensor for hydrogen or humidity. $BaCe_{0.95}Y_{0.05}O_{3-x}$ can detect carbon dioxide as an amperometric-type sensor.[4] Furthermore, $CaZr_{0.9}In_{0.1}O_{3-x}$ is sensitive to various hydrocarbons by means of the catalytic combustion.[5] This paper will describe a new application of protonic conductor to other gases.

A sensor for ethanol is required for examining a drunken driver and controlling a food or fermentation process. As such a sensor, perovskite-type oxide $Ln_{1-x}Sr_xCoO_{3-x}$[6] and semiconductive oxide SnO_2 + CuO[7] have been reported by H. Obayashi et al. and N. Saito et al., respectively. Recently, N. Yamazoe et al. have proposed that Pd-La_2O_3-In_2O_3 thick film element shows excellent ethanol gas sensing properties.[8]

Ethanol is subject to dehydrogenation on basic materials.[9] $BaCeO_3$ oxide is expected to be rather strongly basic from the electronegativities of constituent atoms. If so, this ceramic will be sensitive to ethanol as a consequence of detecting hydrogen produced. In this study, a new type of potentiometric-type sensor for ethanol will be constructed using $BaCe_{0.95}Y_{0.05}O_{3-x}$ ceramic, and its working mechanism will be discussed.

$BaCe_{0.95}Y_{0.05}O_{3-x}$ ceramic was prepared by solid state reaction, followed by sintering. Further details of preparation were described in the previous paper.[10] The ceramic obtained was cut into a thin disc (thickness: 0.5 mm, diameter: 12 mm), which was used as a solid electrolyte for a gas cell. The gas cell was constructed as shown in Fig. 1. Electrode compartments were separated by the solid electrolyte and were

connected to ceramic tubes with glass gaskets. Ag metal was employed as an electrode material. Sample gas and air were introduced into the sensing and counter compartments, respectively, at 723 K, and emf was measured with an electometer. The sample gas was prepared by passing air through a ethanol bubller at a given temperature. The flow rate of gas was 75 ml/min. Composition of outlet gas was determined by a gas chromatography (GC), in which Porapak Q and molecular sieve 5A were used as a column packing.

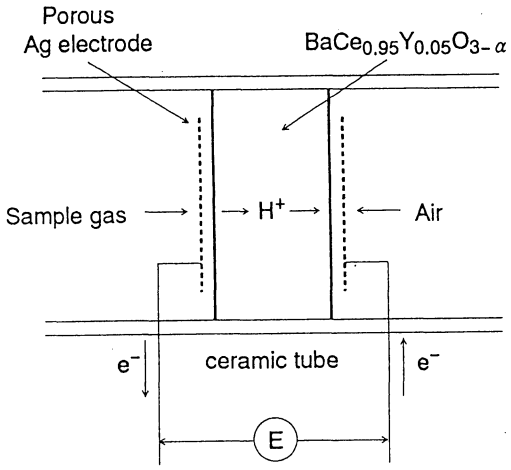

Fig. 1. Schematic illustration of gas cell.

The gas cell gave stable emfs on introducing sample gases with various ethanol concentrations into the sensing compartment, as shown in Fig. 2. The 90% response time on turning-on ethanol was less than 10 s, while that on turning-off ethanol was more than a few minutes, especially at a higher concentration region. The relationship between emf and EtOH concentration is shown in Fig. 3. The emf increased with increasing ethanol concentration, indicating that the gas cell could distinguish ethanol concentrations lower than 2%.

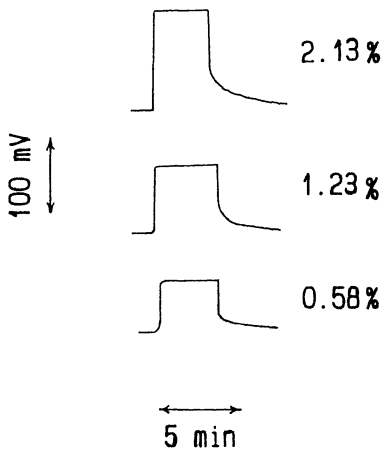

Fig. 2. Response characteristics to ethanol at 723 K.

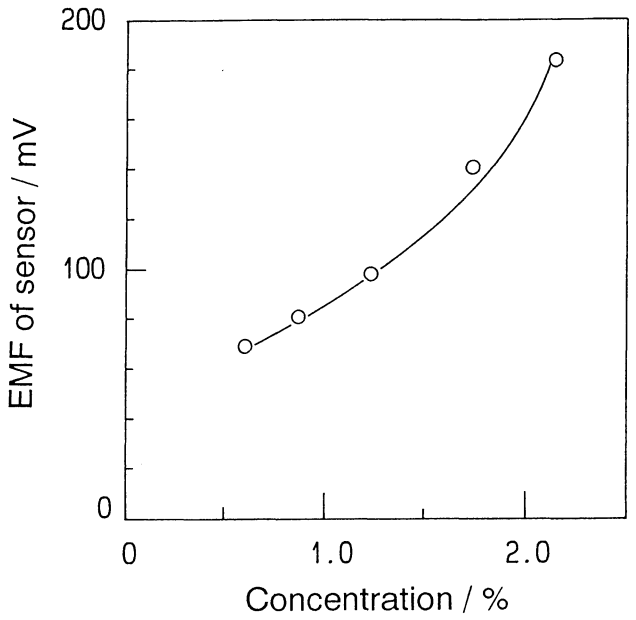

Fig. 3. EMF as a function of concentration of ethanol at 723 K.

The interference of hydrocarbons, CO and water vapor on the detecting of ethanol was then investigated. Emfs generated on introducing various gases into the sensing compartment are summarized in Fig. 4. The gas cell was not so sensitive to CH_4 and C_2H_6, but rather sensitive to C_3H_8, CO and water vapor. However, these emfs were smaller than a value on introducing ethanol with the same concentration. It is necessary to lower the operation temperature so that the afore-mentioned gases do not affect the ethanol sensing.

To understand the mechanism of ethanol sensing better, composition of outlet gas was measured by GC (Table 1). The conversion of ethanol was in the range of 28 to 48%. In addition, H_2 and CH_3CHO were observed as products. These findings indicate that the dehydrogenation of ethanol occurs on the basic material, probably on $BaCe_{0.95}Y_{0.05}O_{3-x}$. According to N. Yamazoe and N. Miura,[11] electrode reactions in (H_2 + air)//proton conductor electrolyte//air cell are proposed as follows.

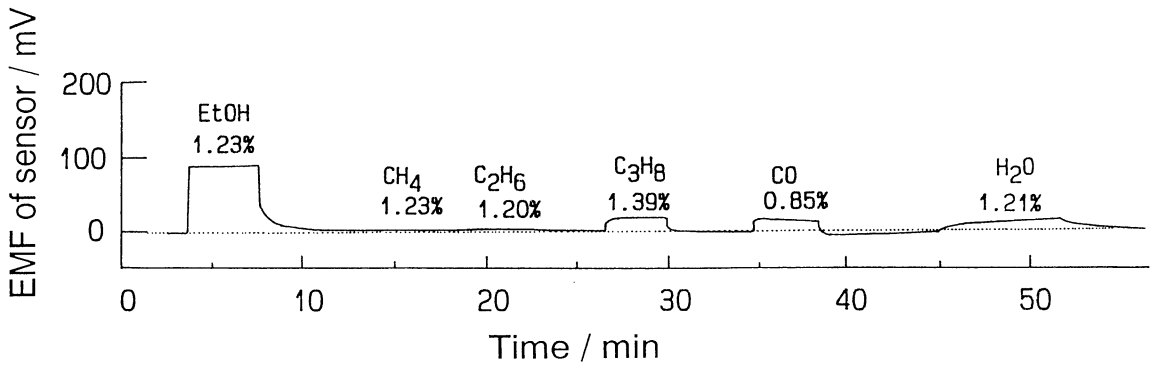

Fig. 4. Response characteristics to inflammable gases and water vapor at 723 K.

Table 1. Activity and distribution of products on $BaCe_{0.95}Y_{0.05}O_{3-x}$.

Concentration of ethanol/%	Conversion/%		Yield/%			
	ethanol	O_2	H_2	CO_2	H_2O	CH_3CHO
0.589	39.8	4.2	0.012	0.158	2.218	0.015
0.845	29.7	4.2	0.017	0.233	3.793	0.022
1.234	28.3	8.0	0.023	0.339	5.157	0.043
1.721	39.7	12.6	0.035	0.523	7.329	0.054
2.131	47.8	20.4	0.066	0.963	8.321	0.117

sensing electrode: $H_2 \longrightarrow 2H^+ + 2e^-$ (1)

$1/2O_2 + 2H^+ + 2e^- \longrightarrow H_2O$ (2)

counter electrode: $1/2O_2 + 2H^+ + 2e^- \longrightarrow H_2O$ (3)

The sensing electrode will be at a mixed potential in which reaction rates of (1) and (2) are equal to each other. In addition, CH_3CHO will react on the sensing electrode, resulting in a mixed potential. Hence, the emf observed will be a difference between such a mixed potential at the sensing electrode and a potential at the counter electrode.

In conclusion, potentiometric-type sensor using $BaCe_{0.95}Y_{0.05}O_{3-x}$ as a solid electrolyte could detect ethanol with the concentration below 2%. The sensing property was ascribed to the dehydrogenation of ethanol.

References

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