SHORT COMMUNICATION

A hydrocarbon sensor using a high temperature-type proton conductor

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1. Introduction

Using a high temperature-type proton conductor as a solid electrolyte, a steam concentration cell can be constructed [1, 2]. When gases with different humidities are introduced into each electrode compartment, this cell gives rise to an electromotive force *E*:

$$E = \frac{RT}{2F}\ln\frac{P_{H_2O(I)}}{P_{H_2O(II)}}\left(\frac{P_{O_2(II)}}{P_{O_2(I)}}\right)^{1/2} \quad (1)$$

where *R*, *F* and *T* have their usual meanings. When $P_{O_2(I)}$ is nearly equal to $P_{O_2(II)}$, the theoretical e.m.f. is determined by the ratio of P_{H_2O} at each electrode.

Based on the principle of such a steam concentration cell, it is possible to make hydrocarbon sensor using a high temperature-type proton conductor. If a material inert to hydrocarbons is attached to one side of the electrolyte and a material which characterizes the combustion of hydrocarbons to another side, as shown in Fig. 1, hydrocarbons included in air will not react on the former, but they will burn to form water vapour and CO_2 on the latter. This situation leads to a steam concentration cell, and this principle can be applied to a hydrocarbon sensor. On the other hand, from the viewpoint of the fact that oxygen is consumed by the combustion of hydrocarbons, an oxygen concentration cell can also be constructed. In this case, the oxide ion conductors must be used as a solid electrolyte.

In the present study, we fabricate two types of hydrocarbon sensors using $CaZr_{0.9}In_{0.1}O_{3-\alpha}$ and yttria stabilized zirconia (YSZ) as proton and oxide ion conductors, respectively, and examine their sensing characteristics. The working mechanism of the sensors is discussed.

2. Experimental procedures

$CaZr_{0.9}In_{0.1}O_{3-\alpha}$ ceramic was prepared by solid state reaction, followed by sintering. The raw materials ($CaCO_3$, ZrO_2 and In_2O_3) were mixed with ethanol and calcined in air at 1673 K for 10 h. The oxide was ground in a ball mill and pressed into the pellet form at $2 \times 10^3\,kg\,cm^{-2}$. The pellet was sintered in air at 1873 K for 10 h. YSZ was prepared by pressing TZ-8Y powder (Tosoh) at $2 \times 10^3\,kg\,cm^{-2}$ and then calcining it at 1823 K for 10 h. The densities of these ceramics were higher than 95% of the theoretical value.

The schematic illustration of the test cell is shown in Fig. 2(a). The ceramic obtained was cut into chip form (8.0 mm × 8.0 mm × 0.5 mm). The $La_{0.6}Ba_{0.4}CoO_3$ electrode was baked on one side of the chip at 1273 K, and then the porous gold electrode on the other side at 973 K. The sensing experiment was carried out in a flow-type apparatus equipped with an electric furnace. The flow rate of the sample gas was $150\,ml\,min^{-1}$. The sample gas was prepared by diluting CH_4, C_2H_6 or C_3H_8 with air. Each hydrocarbon content was less than 3%. The operating temperature was 973 K. The emf of the cell was monitored using an electrometer.

To measure the catalytic activity or the potential of each electrode, a further test cell was constructed as shown in Fig. 2(b). In this case a $CaZr_{0.9}In_{0.1}O_{3-\alpha}$ disc was employed as a solid electrolyte. The porous platinum metal, which was exposed to dry air ($P_{H_2O} = 0.993$ torr), was attached at the top of the disc as a reference electrode. The operating conditions were the same as described above. The analysis of products, except water vapour, was carried out with gas chromatography (GC), in which Prorapak Q and molecular sieve 5A were used as column packing. Water vapour was measured with a humidity sensor.

3. Results and discussion

3.1. *Sensing characteristics for hydrocarbons*

Figure 3 shows the EMFs observed on introducing sample gases with various hydrocarbon contents into the test cell (a). For any hydrocarbon, the e.m.f.

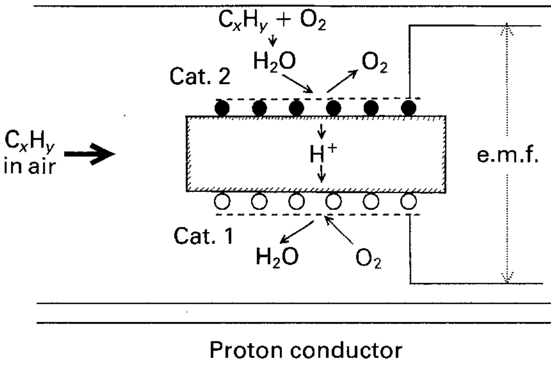

Fig. 1. Principle of hydrocarbon sensor using a proton conductor as a solid electrolyte: cat. 1 and 2 show electrode materials which are inert for hydrocarbons and characterizes their combustion, respectively.

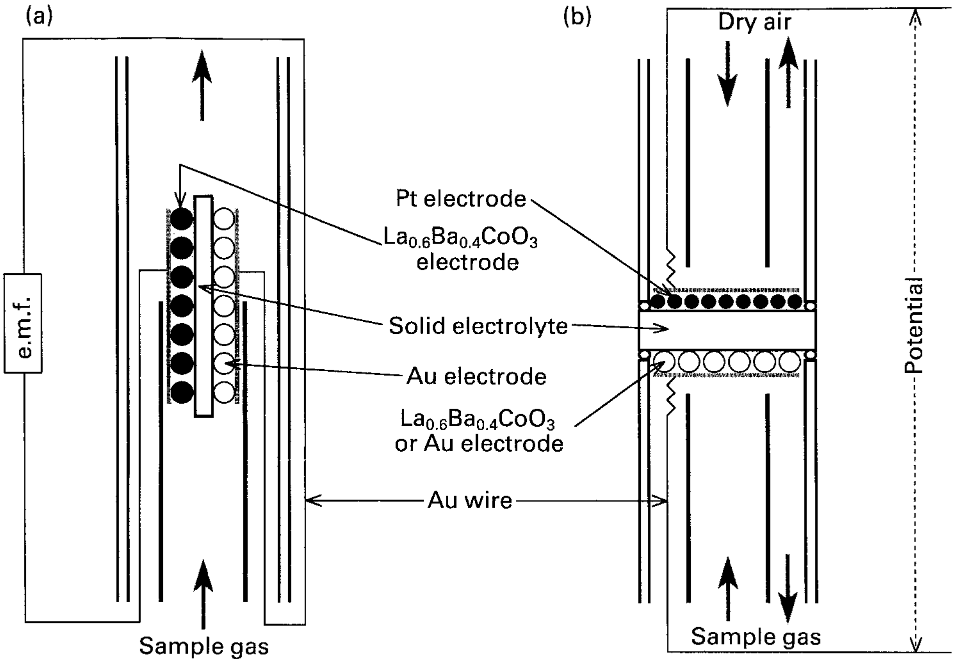

Fig. 2. Schematic illustration of test cells.

increased with increasing content and decreased with decreasing content. The time required to reach 90% of the steady state value was shorter than 5 min. In these cases, the potential of the $La_{0.6}Ba_{0.4}CoO_3$ electrode was negative against the gold electrode. When both two electrodes were gold or $La_{0.6}Ba_{0.4}CoO_3$, the e.m.f. was less than a few millivolt, indicating that these sensing characteristics were based on

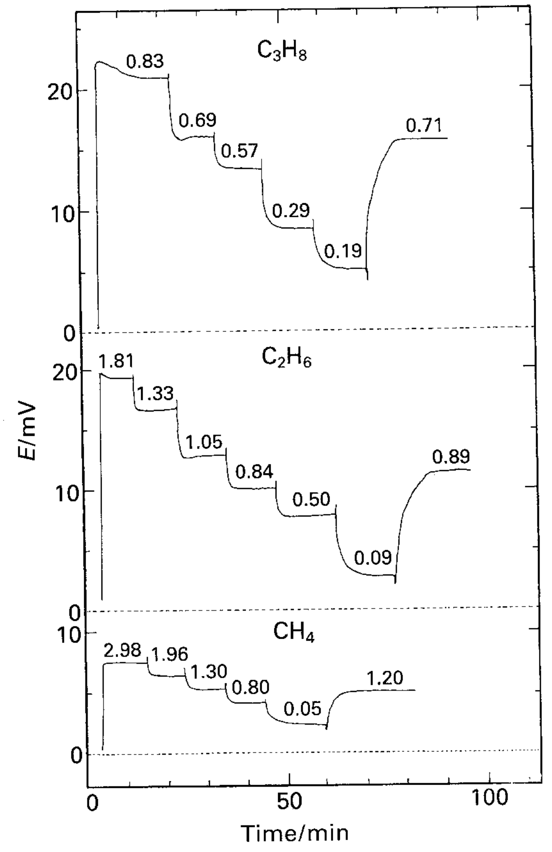

Fig. 3. Change in e.m.f. for sample gases with various hydrocarbon contents in (a): $La_{0.6}Ba_{0.4}CoO_3|CaZr_{0.9}In_{0.1}O_{3-\alpha}|$ Au cell; operating temperature 973 K.

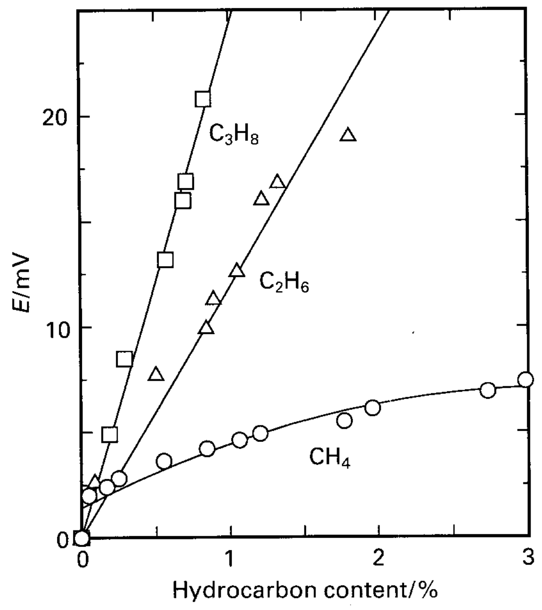

Fig. 4. Plot of e.m.f.'s in test cell (a) against CH_4 (○), C_2H_6 (△) and C_3H_8 (□) contents: $La_{0.6}Ba_{0.4}CoO_3|CaZr_{0.9}In_{0.1}O_{3-\alpha}|$ Au cell; operating temperature 973 K.

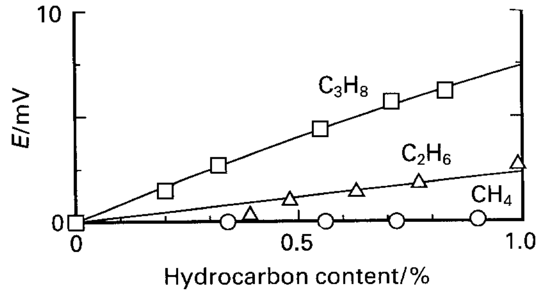

Fig. 5. Plots of e.m.f.'s in test cell (a) against CH_4 (○), C_2H_6 (△) and C_3H_8 (□) contents: $La_{0.6}Ba_{0.4}CoO_3|YSZ|$ Au cell; operating temperature 973 K.

Table 1. Catalytic characterizations of Au and $La_{0.6}Ba_{0.4}CoO_3$ at 700 °C

*Hydrocarbon**	*Au*					
	Reactant			*Conversion*		*Potential vs*
	CH	*O_2*	*H_2O*	*CO_2*	*Others*	*reference electrode*†
	/%	*/%*	*/%*	*/%*	*/%*	*/mV*
CH_4	100	100	0	0	0	+3.8
C_2H_6	100	100	0	0	0	−0.4
C_3H_8	95	100	1	0	0	−3.3
*Hydrocarbon**	*$La_{0.6}Ba_{0.4}CoO_3$*					
	Reactant			*Conversion*		*Potential vs*
	CH	*O_2*	*H_2O*	*CO_2*	*Others*	*reference electrode*†
	/%	*/%*	*/%*	*/%*	*/%*	*/mV*
CH_4	96	99	3	0	0	−6.1
C_2H_6	0	88	99	64	0	−39.2
C_3H_8	0	83	69	100	0	−56.3

* CH_4: 0.90%, C_2H_6: 0.72%, C_3H_8: 0.83%

† Reference electrode was exposed with dry air ($P_{H_2O} = 0.993$ torr).

the combination of gold and $La_{0.6}Ba_{0.4}CoO_3$ electrodes.

The e.m.f.'s observed in the test cell (a) are plotted as a function of CH_4, C_2H_6 and C_3H_8 contents in Fig. 4. Almost linear relationships between e.m.f. and hydrocarbon content were obtained, and the order of the sensitivity was $C_3H_8 > C_2H_6 > CH_4$. From the continuous sensing measurements of the test cell (a), the e.m.f. remained nearly constant above 8 h. Although many high temperature-type proton conductors so far reported react easily with CO_2 to decompose to carbonates, $CaZr_{0.9}In_{0.1}O_{3-\alpha}$ has been found to be very stable to CO_2 [2].

The test cell (a) was constructed using YSZ as a solid electrolyte. This cell also responsed to hydrocarbons in a similar manner as above, but the e.m.f.'s were smaller, as shown in Fig. 5.

3.2. *Sensing mechanism*

To understand the sensing mechanism of these cells, the catalytic activity of each electrode was studied using the test cell (b). The results are summarized in Table 1. The gold electrode scarcely exhibited any catalytic activity for the combustion of hydrocarbons. In addition, the potential of the gold electrode was small. On the other hand, in the outlet gases of the $La_{0.6}Ba_{0.4}CoO_3$ electrode compartment, hydrocarbons, especially C_2H_6 and C_3H_8, disappeared, and oxygen was partially consumed. Water vapour and CO_2 were formed as a product. In addition, a large potential was observed against the reference electrode. From these facts, it is expected that the ratio of P_{H_2O} at two electrodes in the test cell (a) is large, so that a stable e.m.f. is given using $CaZr_{0.9}In_{0.1}O_{3-\alpha}$ as a solid electrolyte. However, since the ratio of P_{O_2} at two electrodes is small, the e.m.f. is poor in the case of YSZ.

4. Conclusion

Using a $CaZrO_3$-based proton conductor as a solid electrolyte, a hydrocarbon sensor has been constructed. The test cell with gold metal and $La_{0.6}Ba_{0.4}CoO_3$ oxide as electrode material gives rise to stable e.m.f.'s on introducing air containing hydrocarbons (CH_4, C_2H_6 or C_3H_8). This sensing mechanism is based on a steam concentration cell, which results from the difference in combustion activity for hydrocarbons between two electrode materials.

References

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[2] T. Yajima, H. Iwahara, K. Koide and K. Yamamoto, *Sensors and Actuators Chemical, B* **5** (1991) 145.