A novel approach for gasification of carbon using a mixed conductor

T. SHIMURA, M. ITOH, H. IWAHARA

Center for Integrated Research in Science and Engineering, Nagoya University, Furo-cho Chikusa-ku, Nagoya 464-01, Japan

The gasification of carbon to CO without the production of nitrogen was studied using an oxide ionic and electronic mixed conductor. The oxide ionic and electronic mixed conductor $CaTi_{0.75}Fe_{0.25}O_{3-\alpha}$ was used as a selective oxygen permeable diaphragm. The selective electrochemical permeation of oxygen across a ceramic sample was confirmed by measuring oxygen evolution rate at the low P_{O_2} side of the oxygen gas concentration cell using sample ceramics as a diaphragm. The gasification of carbon black to CO using this diaphragm was examined. It was observed that CO and CO_2 were formed without nitrogen when the opposite side of diaphragm was exposed to air at high temperature. The dependence of the CO/CO_2 ratio on the partial pressure of oxygen in the high P_{O_2} compartment and on the thickness of diaphragm was examined.

1. Introduction

The gasification of carbon sources such as coal and petroleum cokes is desirable for effective and convenient utilization of fuels. Efforts have been made to gasify such materials by partial oxidation (or partial combustion) methods [1, 2]. If air is used in these processes, the gas formed includes nitrogen gas, formed in twice the volume of the carbon monoxide produced. As a result, the calorific value of the fuel gas is low because of dilution. To avoid this, pure oxygen gas must be used as the partial oxidant. This means, however, a complicated oxygen gas production plant is necessary, which makes the product gas expensive.

In this study we propose a new electrochemical method for carbon gasification avoiding the production of nitrogen. This method uses an oxide ionic and electronic mixed conducting ceramic as a functional diaphragm. Figure 1(a) shows the equivalent circuit of the mixed conductor under oxygen gas concentration cell condition. At high temperature, if the oxygen partial pressure of each side of the diaphragm is different, the mixed conductor selectively passes oxygen spontaneously. The principle of the gasification method is illustrated in Fig. 1(b). When one side of a mixed conductor is exposed to air and the other side to carbon at elevated temperature, oxygen permeates electrochemically across the mixed conductor from the air to the carbon side.

air side:

$$\tfrac{1}{2}O_2 + 2e^- \rightarrow O^{2-} \qquad (1)$$

carbon side:

$$O^{2-} + C \rightarrow CO + 2e^- \qquad (2)$$
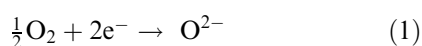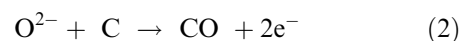
Based on this principle, we examined the gasification of carbon to CO gas using air as partial oxidant but free from N_2 or NO_x at high temperature. The advantage of using a mixed conductor electrolyte for electrochemical gasification is the simplification of the apparatus. The outer electrical circuit and electrodes are not necessary, although this method is based on an electrochemical process. Therefore, the gasification apparatus is constructed only with a diaphragm or tube of the mixed conductor and a furnace.

The oxide ion and electron mixed conductor used in this study was perovskite-type oxide composed of $CaTi_{0.75}Fe_{0.25}O_{3-\alpha}$. Studies on oxide ion and electron mixed conduction in several kinds of perovskite-type oxides have been reported [3–7]. These oxides contain transition metals such as cobalt [3–6], manganese [3], iron [4] and chromium [7] at B-site. High temperature superconductive copper oxide $LnBa_2Cu_3O_x$ (Ln = rare earth metal) also exhibits oxide ion and electron mixed conduction [8]. All these compounds, however, are not suitable for the gasification method proposed in this study due to thermal instability under reducing atmosphere at high temperature or due to the poor mechanical strength.

The thermal stability under reducing atmosphere and the oxide ion and electron mixed conduction in $CaTi_{1-x}Fe_xO_{3-\alpha}$ was confirmed [9, 10] earlier and the separation of oxygen from air using $CaTi_{1-x}Fe_xO_{3-\alpha}$ was reported by one of the present authors [9].

2. Experimental details

Samples of $CaTi_{0.75}Ti_{0.25}O_{3-\alpha}$ ceramic were prepared by the conventional solid state reaction method. Raw materials were $CaCO_3$, TiO_2 and Fe_2O_3, respectively. A stoichiometric amount of powders of raw materials mixed in an agate mortar with ethanol was calcined at 1250 °C in air for 12 h. Furnace-cooled samples were reground in an agate mortar and in a ball mill. Reground powder was pressed into pellet-shapes under an isostatic pressure of 230 MPa. The pellet was sintered at 1500 °C in air for 12 h. The single phase of the sample was confirmed by powder X-ray diffraction analysis.

The oxygen transport properties of $CaTi_{0.75}$-$Ti_{0.25}O_{3-\alpha}$ were investigated using electrochemical permeation of oxygen at elevated temperature. As shown in Fig. 2, a thin disc of specimen mixed conductor (13 mm diam. × 1 mm thick) was sandwiched between two alumina tubes via glass packings making a cell with two compartments. The oxygen gas permeation rate was determined by measuring the content of oxygen in argon gas from one compartment of the cell as a function of P_{O_2} in another compartment. A zirconia-type oxygen sensor was used for measurement of oxygen and gas chromatography for checking the absence of nitrogen gas.

To determine the transport number of the oxide ion and the impedance of the cell, porous platinum electrodes were attached to the centre of each surface of the specimen disc and the e.m.f. of the oxygen concentration cell using the disc as a solid electrolyte was measured. The details of the measurement are shown elsewhere [9].

$$E_o = \frac{RT}{4F} \ln \frac{P_{O_2}(low)}{P_{O_2}(high)}$$

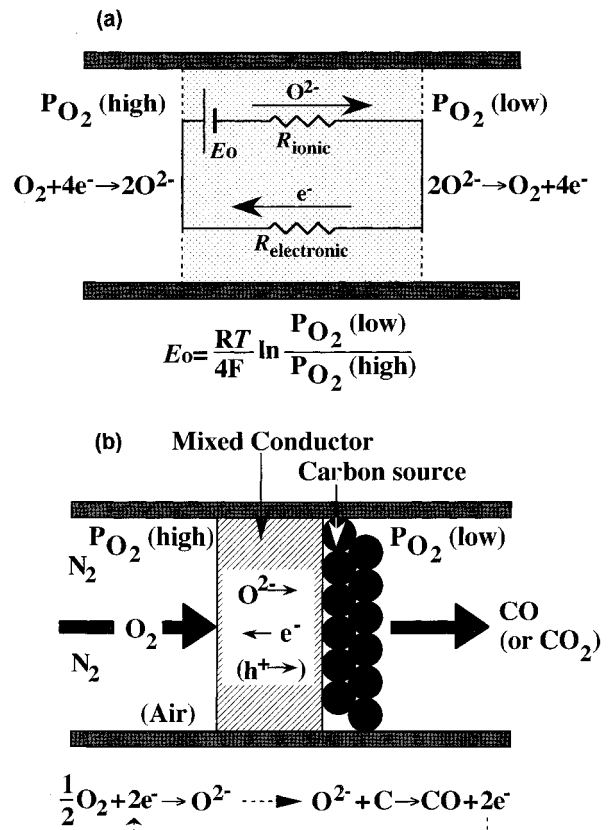$$\frac{1}{2}O_2 + 2e^- \to O^{2-} \quad \dashrightarrow \quad O^{2-} + C \to CO + 2e^-$$

Fig. 1. (a) Equivalent circuit of mixed conductor under concentration cell condition. (b) The principle of carbon gasification using oxide ionic and electronic mixed conducting diaphragm.

The gasification of carbon was examined using the same apparatus as shown in Fig. 2. In this case, as a carbon source, the carbon black was directly mounted on the mixed conductor disc as shown in
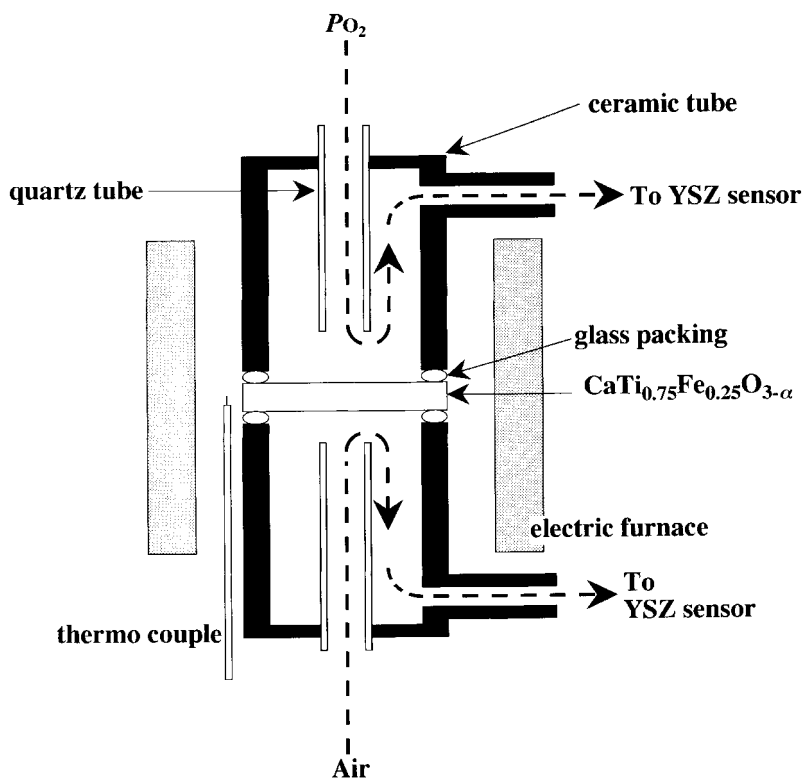

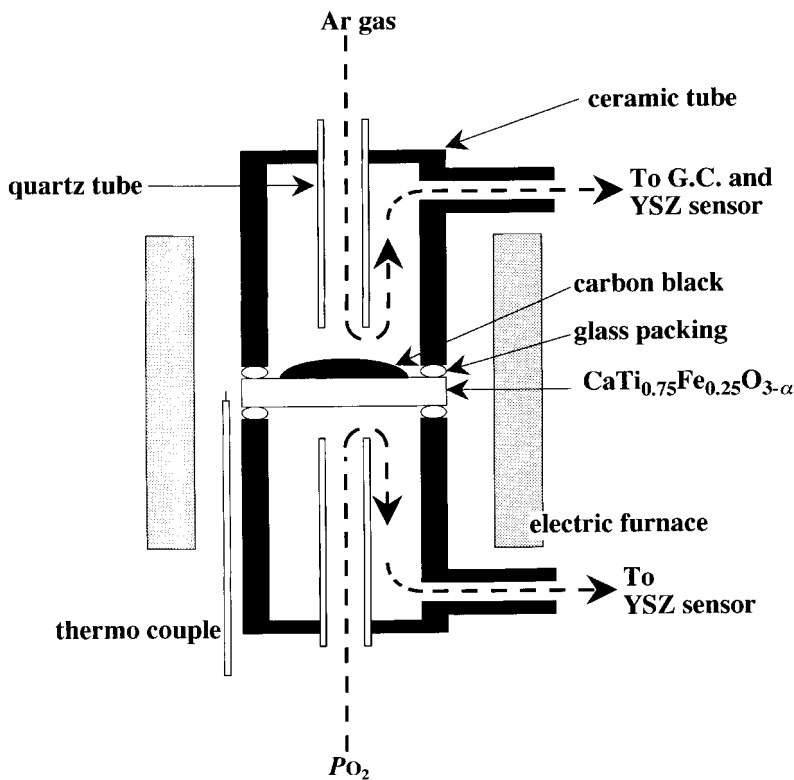Fig. 2. Cell for electrochemical oxygen permeation experiment.

Fig. 3. Cell for gasification experiment.

Fig. 3 and air was supplied to the lower side of the disc. In order to carry the formed gas around the carbon on the upper side of the disc, argon gas was passed through the upper compartment and the exit gas was analysed by gas chromatography. Thus, the formation rate of CO and CO_2 and the evolution rate of O_2 and N_2 were measured under different experimental conditions.

## 3. Results and discussion

3.1. Conduction properties

The dense ceramic of $CaTi_{0.75}Fe_{0.25}O_{3-\alpha}$ was obtained by sintering at 1500 °C. The relative density of the ceramic was more than 95%. The single phase structure of the ceramic sample was confirmed by the powder X-ray diffraction at room temperature. The crystal structure of $CaTi_{0.75}Fe_{0.25}O_{3-\alpha}$ was distorted perovskite, although the distortion from cubic to orthorhombic symmetry was smaller than that in $CaTiO_3$.

Figure 4 shows the electrical conductivity of $CaTi_{0.75}Fe_{0.25}O_{3-\alpha}$ at 1000 °C as a function of oxygen partial pressure, P_{O_2}, at one side of the disc, keeping P_{O_2} at the other side constant (air). The dependence of conductivity on P_{O_2} was not so marked as in the case of a homogeneous atmosphere reported earlier [9].

Ionic transport numbers in $CaTi_{0.75}Fe_{0.25}O_{3-\alpha}$, determined from the e.m.f. of the oxygen concentration cell at 1000 °C, are shown in Fig. 5 as a function of the oxygen partial pressure. The dependence of transport numbers on P_{O_2} was small at 1000 °C as expected from that in Fig. 4.

3.2. Electrochemical oxygen permeation

Evolution of oxygen gas was observed at the argon gas side of the specimen diaphragm when air was supplied to the lower side and Ar to the upper side (Fig. 2). Figure 6 shows the oxygen evolution rates at various temperatures. The rapid increase in evolution
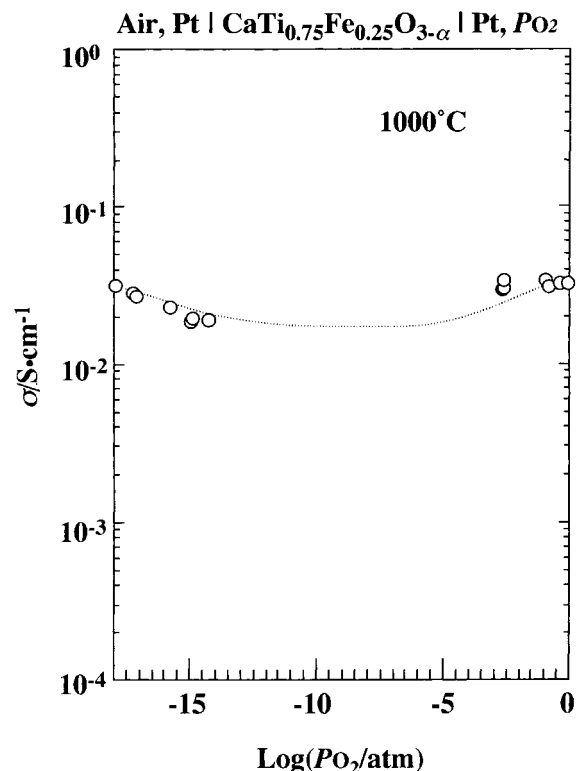
Fig. 4. Electrical conductivity of $CaTi_{0.75}Fe_{0.25}O_{3-\alpha}$ as a function of the oxygen partial pressure at 1000 °C.
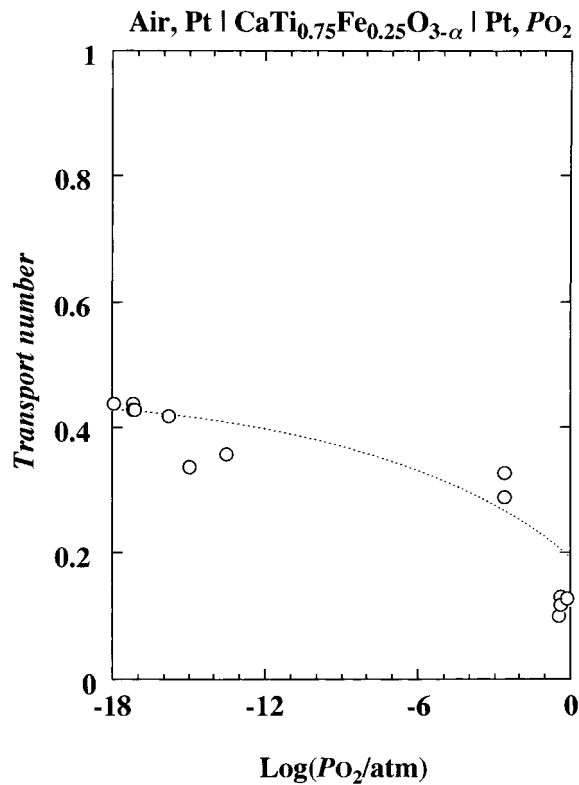
Air, Pt | CaTi$_{0.75}$Fe$_{0.25}$O$_{3-\alpha}$ | Pt, PO$_2$

Fig. 5. Ionic transport number of CaTi$_{0.75}$Fe$_{0.25}$O$_{3-\alpha}$ determined from E/E_0 as a function of oxygen partial pressure at anode at 1000 °C. Here, E and E_0 denote the observed and theoretical e.m.f. of oxygen concentration cells, respectively.
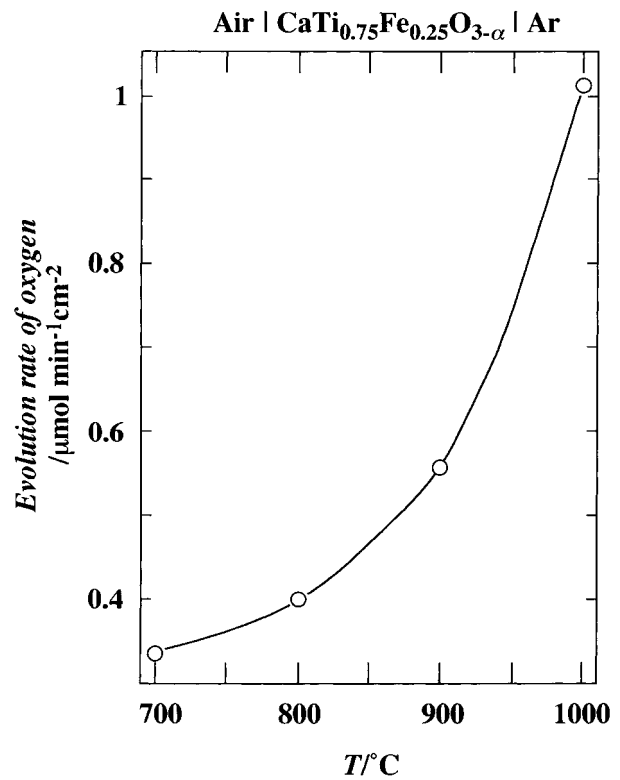
Air | CaTi$_{0.75}$Fe$_{0.25}$O$_{3-\alpha}$ | Ar

Fig. 6. Oxygen evolution rate at the argon side of the cell at various temperatures, air |CaTi$_{0.75}$Fe$_{0.25}$O$_{3-\alpha}$|Ar. (Diaphragm thickness: 1.0 mm).

rate with temperature is due to the increased conductivity. This means that high operating temperature is necessary for effective carbon gasification. The evolution of nitrogen gas was not detected, indicating that oxygen permeated selectively through the mixed conductor diaphragm. This result also means that there was no mechanical leakage of gas through grain boundaries or microcracks in the diaphragm.

Figure 7 shows the observed oxygen evolution rates at 1000 °C as a function of oxygen partial pressure on the low P_{O_2} side. The dotted line represents the values calculated from Equation 3:

$$V_c = \frac{15RT(1 - t_i)\sigma_i}{4F^2l}\ln\frac{P_{O_2}(\text{high})}{P_{O_2}(\text{low})} \text{ mol min}^{-1}\text{ cm}^{-2}$$

$$(3)$$

where R, T and F have their usual meanings and P_{O_2}, σ_i, t_i and l are oxygen partial pressures, ionic conductivity, transport number of oxide ion and disc thickness, respectively. Here, σ_i, and t_i were adopted from the values shown in Figs 4 and 5. A similar dependence on the oxygen partial pressure appeared in both experimental and calculated evolution rates, although the experimental values were somewhat lower than the calculated.

3.3. Gasification of carbon

In the gasifier experiment, the following four reactions are considered to occur in the carbon black compartment.
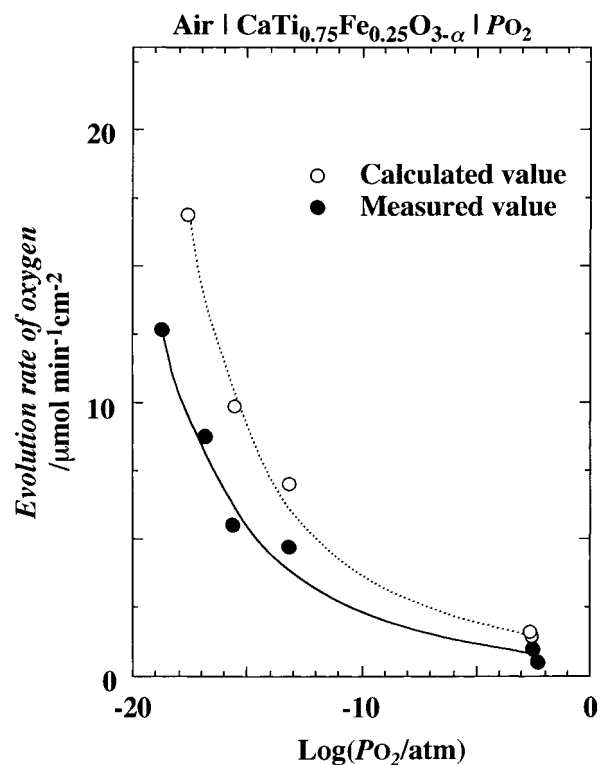
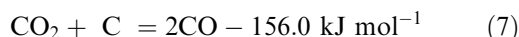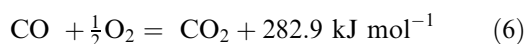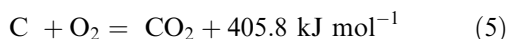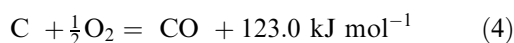**Air | CaTi$_{0.75}$Fe$_{0.25}$O$_{3-\alpha}$ | PO$_2$**

Fig. 7. Oxygen evolution rate at low oxygen partial pressure side as a function of its P_{O_2} (1000 °C, another side: air, thickness of the specimen: 1.0 mm). Closed circles express the experimental values and open circles express the values calculated from the conductivity and transport number of the oxide ion using Equation 3.

$$C + \tfrac{1}{2}O_2 = CO + 123.0 \text{ kJ mol}^{-1} \qquad (4)$$

$$C + O_2 = CO_2 + 405.8 \text{ kJ mol}^{-1} \qquad (5)$$

$$CO + \tfrac{1}{2}O_2 = CO_2 + 282.9 \text{ kJ mol}^{-1} \qquad (6)$$

$$CO_2 + C = 2CO - 156.0 \text{ kJ mol}^{-1} \qquad (7)$$

Although Reaction 7 is endothermic, the total reaction to form carbon monoxide expressed as Equation 4 is exothermic.

Formation of carbon monoxide and carbon dioxide at the upper side of the cell shown in Fig. 3 were confirmed by analysing the exit argon gas with gas chromatography. The results are shown in Figs 8 and 9 as functions of oxygen partial pressure and thickness of the mixed conductor, respectively.

The dependence of CO and CO_2 formation rates on oxygen partial pressure in the high P_{O_2} compartment at 1000 °C are shown in Fig. 8. The formation rate of CO markedly increased as the oxygen partial pressure on the high P_{O_2} side increased, but the evolution rate of CO_2 showed little change. When the high P_{O_2} side gas was air and the carbon side gas was argon, the formation rate of CO was almost twice that of CO_2 under the same conditions.

Figure 9 shows the dependence of the CO and CO_2 formation rates on sample thickness at 1000 °C. The formation rate of CO largely increased as the thickness decreased. This increase was compatible with the calculated dependence of the oxygen evolution amount on diaphragm thickness. On the other hand,
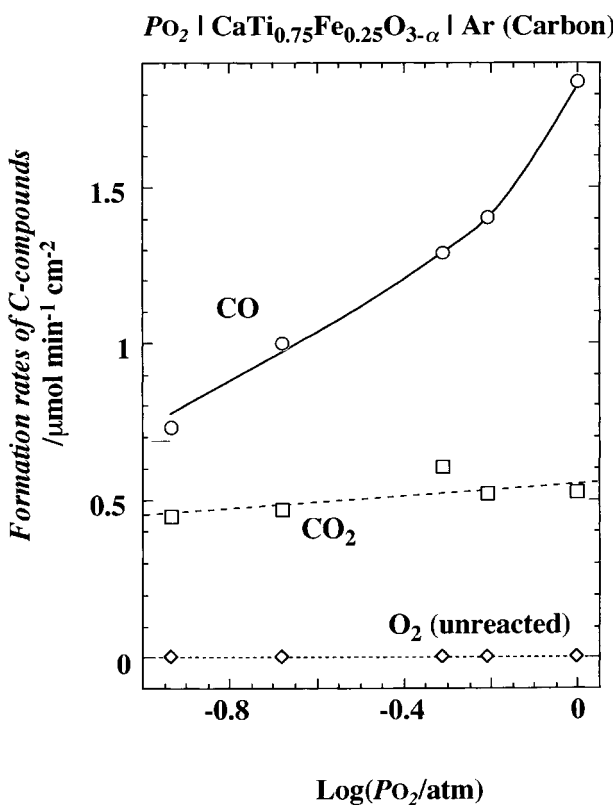
Air I CaTi$_{0.75}$Fe$_{0.25}$O$_{3-\alpha}$ I Ar (Carbon)

Fig. 9. Formation rate of CO and CO_2 as a function of diaphragm thickness at 1000 °C.

the CO_2 formation rate was almost independent of thickness. As a result, the ratio CO/CO_2 largely increased as the thickness decreased.

Unreacted oxygen was not detected in the Ar in the gasification experiment. Neither N_2 or NO_x were detected in the exit gas, indicating that there were no pores through which molecular nitrogen from the air permeated. This means that oxygen permeates electrochemically across the mixed conductor.

As suggested from the dependence of conductivity on temperature, and as shown in Fig. 6, a high operation temperature is desirable for effective oxidation of carbon in the carbon compartment. Reduced diaphragm thickness is also desirable for effective gasification as shown in Fig. 9. The high temperature such as 1000 °C can be attained by heat management since the total reaction of this cell is exothermic. In contrast to a high temperature solid state electrolyte fuel cell, the construction of the cell is simple and no gas sealing technique is necessary if tubes of the mixed conductor are available. Reducing the diaphragm thickness requires good mechanical strength. This might be achieved by coating the mixed conductor film on a porous substrate [11].

P_{O_2} I CaTi$_{0.75}$Fe$_{0.25}$O$_{3-\alpha}$ I Ar (Carbon)

Fig. 8. Formation rates of CO and CO_2 as functions of oxygen partial pressure in the high P_{O_2} compartment at 1000 °C. (Diaphragm: thickness 1.0 mm).

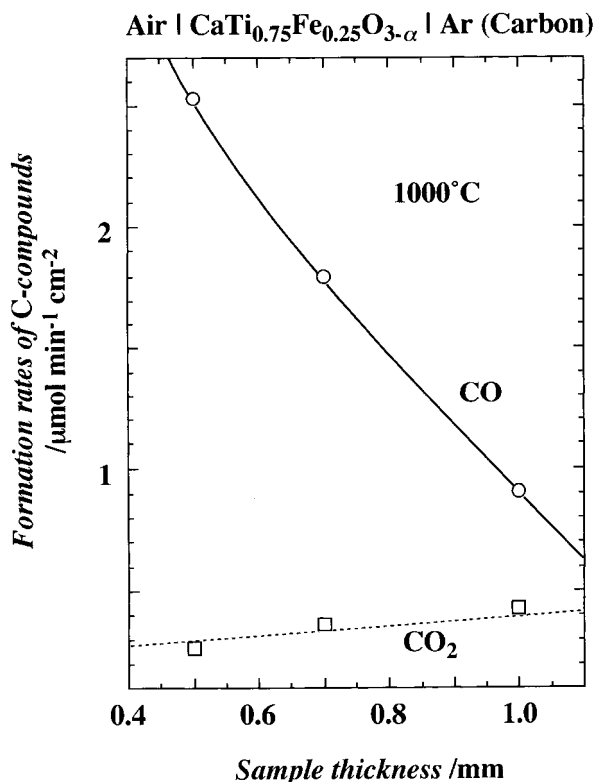## 4. Summary

The selective permeation of oxygen across a Ca-Ti$_{0.75}$Fe$_{0.25}$O$_{3-\alpha}$ ceramic diaphragm was examined at high temperature. It was observed that only oxygen evolved at the low P_{O_2} side of the diaphragm. The

dependence of permeation rate on partial pressure of oxygen obeyed the estimated curve from the measured conductivity and transport number under each condition, although the values themselves were somewhat low compared to the calculated values.

The gasification of carbon black using the oxide ion and electron mixed conductor $CaTi_{0.75}Fe_{0.25}O_{3-\alpha}$ was examined and carbon monoxide and carbon dioxide were formed without contamination of nitrogen gas. Both the absolute formation rate of CO and the ratio of CO/CO_2 increased as the thickness of the diaphragm decreased and as the oxygen partial pressure difference between the two sides of the specimen disc increased.

Acknowledgement

References

[1] K. Hashimoto, *Energy and Resources* **13** (1991) 247.
[2] C. Song, H. H. Schobert and A. W. Scaroni, *ibid.* **15** (1994) 142.
[3] S. Carter, A. Selcuk, R. J. Chater, J. A. Kilner and B. C. H. Steele, *Solid State Ionics* **53–56** (1992) 597.
[4] L. Qiu, T. H. Lee, L.-M. Liu, Y. L. Yang and A. J. Jacobson, *ibid.* **76** (1995) 321.
[5] V. V. Kharton, E. N. Naumovich, A. V. Nikolaev, *ibid.* **83** (1996) 301.
[6] V. V. Kharton, E. N. Naumovich, A. A. Vecher and A. V. Nikolaev, *J. Solid State Chem.* **120** (1995) 128.
[7] V. E. J. van Dieten, J. P. Dekker and J. Schoonman, *Solid State Ionics* **53–56** (1992) 611.
[8] M. V. Patrakeev, I. A. Leonidov and V. L. Kozhevnikov, *ibid.* **82** (1995) 5.
[9] H. Iwahara, T. Esaka and T. Mangahara, *J. Appl. Electrochem.* **18** (1988) 173.
[10] T. Esaka, T. Fujii, K. Suwa and H. Iwahara, *Solid State Ionics* **40/41** (1990) 544.
[11] H. Itoh, H. Asano, K. Fukuroi, M. Nagata and H. Iwahara, *J. Amer. Ceram. Soc.* **80** (1997) 1359.