Oxidative coupling of CH_4 using alkali-metal ion conductors as a solid electrolyte

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The oxidative coupling of CH_4 to C_2H_4 and C_2H_6 (C_2-hydrocarbons) has been carried out using an Li^+ ion conductor as a solid electrolyte. A single-compartment cell is constructed from $(Li_2O)_{0.17}(BaO)_{0.07}(TiO_2)_{0.76}$ (LBT) ceramic with two gold electrodes. Alternative current voltages are applied between the two electrodes with a mixture of 8.3% CH_4 and 1.6% O_2 in argon. The experiments are carried out under various conditions. The formation of C_2-hydrocarbons is the most effectively enhanced at a temperature of 850 °C or a frequency of 10 Hz. For example, the conversion of CH_4 and the selectivity of C_2-hydrocarbons at 3 V are 2 and 1.5 times more than those at the open circuit, respectively. The applications of a dc voltage to a two-compartment cell suggested that the active sites are generated *via* the cathodic reaction. The mechanism for the formation of C_2-hydrocarbons is discussed in detail.

Since the discovery of the oxidative coupling of CH_4 (OCM) by Kelly and Bhasin,[1] many papers have been reported concerning the preparations of the selective catalysts and the mechanisms of the OCM reactions. The OCM reaction offers an advantage of having a 'one-step' process to obtain C_2H_4 and C_2H_6 (C_2-hydrocarbons). The one-step process for C_2H_4 as follows:

$$2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O \qquad (1)$$

In the OCM reaction using ion conductors as solid-oxide membranes, fluorite-type oxide ion conductors[2–7] and perovskite-type proton conductors[8–10] have shown appreciably high selectivities to C_2-hydrocarbons, but, so far, other ion conductors have not been applied. However, as some of the selective catalysts to the OCM reaction consist of the oxides of alkaline-metals such as Li_2O[11] and Na_2O,[12] the application of these ion conductors to the solid-oxide membranes for the OCM reaction are expected. In this case, unfortunately, there arises a serious problem in that the alkaline-metal ion conductors are rapidly polarized under a dc voltage resulting in their destruction. Recently, we have proposed that the oxide ion conductor, YSZ ceramic, can be operated as a solid-oxide membrane not only under a dc voltage but also under an ac voltage.[13] If an ac voltage with an adequate frequency is applied to the alkaline-metal ion conductor, these ions will transfer between the two electrodes without their polarization.

However, most membrane reactors for the OCM reaction have been constructed as two-compartment cells, in which CH_4 and O_2 are fed to opposite sides of the solid-oxide membrane. The main disadvantages are that a high temperature gas seal is required and that a carbon deposition occurs on the electrode in the CH_4 compartment. As an alternative, a single-compartment cell has been used, in which both the electrodes are exposed to a mixture of CH_4 and O_2. This design can easily solve the two above-mentioned problems. In this study, single-compartment cells with some alkaline-metal ion conductors are constructed as shown in Fig. 1(a), where an ac voltage is applied between the two electrodes in order to enhance the formation of C_2-hydrocarbons from CH_4 *via* the OCM reaction.

Experimental

The alkali-metal ion conductors used in this study were $(Li_2O)_{0.17}(BaO)_{0.07}(TiO_2)_{0.76}$ (LBT) and $Li_{1.8}Mg_{0.1}TiO_3$ (LMT) as Li^+ ion conductors and β-alumina as an Na^+ ion conductor. The former two ceramics were prepared by solid-state reactions of the oxides or the carbonates, followed by sintering. Further details of their preparations have been described in previous studies.[14,15] The β-alumina ceramic was donated from NGK (Japan). The other ion conductors in control experiments were YSZ (8 mol% Y_2O_3) as an oxide ion conductor and $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ (SCY) as a proton conductor. Their preparation methods were similar to those already reported.[10,13]

A single-compartment cell is schematically shown in Fig. 1(a). The ion conductive ceramic was sliced into the form of a disc (12 mm diameter and 0.55 mm thickness). Two gold electrodes, in the form of a porous film (about 10 µm thickness and 0.5 cm^2 area), were attached to the left and right faces of the disc by heating them at 850 °C for 1 h. The cell obtained was placed in an alumina tube, and two gold wires from the two electrodes were connected with a potentiostat, which could supply ac voltages with the frequency region of 0.1–10^6 Hz. The reaction was carried out by passing a mixture of 8.3% CH_4 and 1.6% O_2 in Ar at a rate of 24 cm^3 min^{-1} between

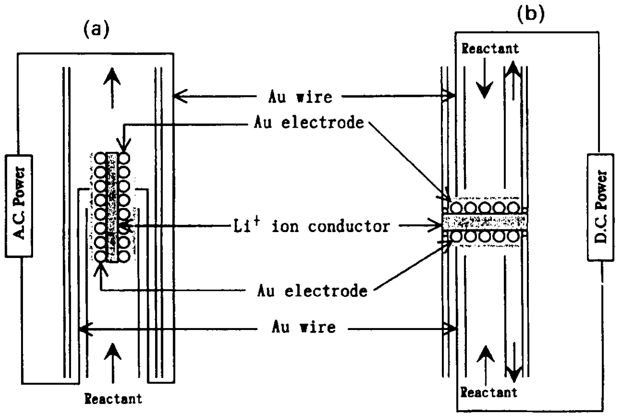

Fig. 1 Schematic illustrations of two kinds of test cells

800 and 900 °C. Compositions of the inlet and outlet gases were analysed by gas chromatography, in which Porapak Q and molecular sieve 5A were used as column packings.

A two-compartment cell was used in order to separate the anodic and cathodic reactions, as shown in Fig. 1(b), where dc voltages were applied to the cell. The disc of the LBT ceramic served as a membrane diaphragm, and the two gold electrodes were attached to the top and bottom faces of the disc. The two CH_4–O_2 mixtures with the above composition were fed to the two compartments at 850 °C. The other experimental conditions were the same as those described above.

Results and Discussion

Typical results for the OCM reaction using various ionic conductors as solid-oxide membranes at 850 °C are summarized in Table 1. C_2H_4, C_2H_6, CO_2 and trace amounts of CO were observed in the outlet gas from all reactors under the open-circuit conditions, where there were little differences in conversion of CH_4 and selectivity to C_2-hydrocarbons among the ionic conductor species. It is likely that the OCM reaction at the open circuit occurs on the surfaces of the two gold electrodes. On the other hand, the OCM reaction under an ac voltage of 3 V at a frequency of 10 Hz was dependent on the ionic conductor species. For the alkaline-metal ion conductors, the catalytic activities and the C_2-selectivities were higher than those under the open-circuit conditions. In particular, LBT showed 2 and 1.5 times higher CH_4 conversion and C_2-selectivity than at the open circuit, respectively. For the oxide ion and proton conductors, however, the catalytic activities and the C_2-selectivities were little affected. Hence, in subsequent experiments, we chose the LBT membrane with the highest catalytic activity and C_2-selectivity and studied its behaviour as a solid-oxide membrane in detail.

Fig. 2 shows the effects of temperature on the formation rates of the products and the C_2-selectivity. The experiment was carried out between 800 and 900 °C. The r/r_0 shown in Fig. 2 is the enhancement ratio of the formation rates of the products under an ac voltage of 3 V at a frequency of 10 Hz to the open-circuit values. The r/r_0 value of C_2H_4 was the largest among those of all products in the temperature region studied, indicating that application of an ac voltage to the LBT membrane specifically enhances the formation of C_2H_4. On the other hand, the r/r_0 values of C_2H_4 had a maximum at 850 °C. The decrease in r/r_0 value of C_2H_4 at 900 °C is not due to the reaction path (the burning rate of C_2H_4 exceeds its formation rate at 900 °C), but because the r/r_0 value of CO_2 at 900 °C is close to unity. This suggests that a favourable species for the formation of C_2H_4 is effectively generated at *ca.* 850 °C.

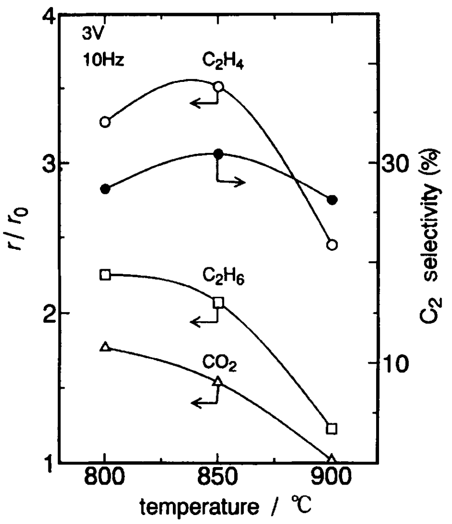

Fig. 2 Effect of temperature on formation rates of products and C_2-selectivity: reactant 8.3% CH_4 and 1.6% O_2 in Ar; flow rate 24 ml min^{-1}, ac voltage 3 V; frequency 10 Hz

Fig. 3 shows the effect of ac voltage on the formation rates of the products and the C_2-selectivity. The experiment was carried out below 3 V in order to depress the heat evolution due to the ohmic resistance of the LBT membrane. The r/r_0 values of all products became larger as the ac voltage increased, and the voltage effect was remarkable, especially above 1 V. This is different from those observed by applying dc voltages to the YSZ membranes, where the r/r_0 value of C_2-hydrocarbons has a maximum at moderate voltages and decreased at greater voltages.[2–7] This is because the excess oxygen pumping through the YSZ membrane generates the gas-phase oxygen with less C_2-selectivity. The application of

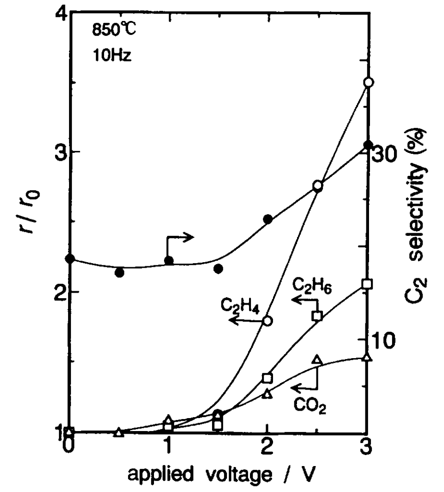

Fig. 3 Effect of ac voltage on formation rates of products and C_2-selectivity: reaction temperature 850 °C; experimental conditions as in Fig. 2

Table 1 Oxidative coupling of CH_4 using various ionic conductors as solid-oxide membrane

	open circuit						application of ac 3 V					
	formation rate /µmol min^{-1} cm^{-2}				conv. (%)	selec. (%)	formation rate /µmol min^{-1} cm^{-2}				conv. (%)	selec. (%)
	C_2H_4	C_2H_6	CO_2	CO	CH_4	C_2	C_2H_4	C_2H_6	CO_2	CO	CH_4	C_2
YSZ	0.67	0.81	5.41	trace	5.04	19.6	0.78	0.73	5.41	trace	5.13	19.9
SCY	0.99	0.99	6.79	trace	6.58	21.1	1.04	1.12	7.12	trace	6.87	21.8
β-Al_2O_3	0.66	0.77	5.91	trace	4.65	17.9	0.63	0.83	6.02	trace	4.79	18.1
LMT	0.98	1.09	6.37	trace	6.27	24.5	1.69	1.49	7.99	trace	8.81	28.4
LBT	0.67	0.78	6.35	trace	5.51	18.6	2.36	1.62	8.90	trace	10.2	30.9

Experimental conditions: temperature, 850 °C; reactant, 8.3% CH_4 + 1.6% O_2 (Ar balance) 24 cm^3 min^{-1}; ac voltage, 3 V; frequency, 10 Hz.

ac voltages to the LBT membrane does not generate such an unfavourable species for the formation of C_2-selectivity even at greater voltages.

Fig. 4 shows the effect of frequency on the formation rates of the products and the C_2-selectivity. The experiment was carried out between 0.1 and 10^6 Hz at an ac voltage of 3 V. At the same time, the impedance of the LBT membrane was measured as shown in Fig. 5. At 10^6 Hz, the formation rates of all products were almost the same as those at the open circuit, and the impedance was close to the real (Z') axis value of the complex impedance plot. These results indicate that most of Li^+ ions exist in the bulk of LBT and, thus, cannot improve the OCM reaction. As the frequency decreased from 10^5 Hz to 0.1 Hz, the formation rates of all products became progressively larger, and the maxima in the curves were observed around 10 Hz. The impedance plot observed under the operating condition consisted of a single arc owing to the transfer of Li^+ ions from the electrolyte to the electrode. In this case, the overall electrode reaction which takes place at the electrode can be presumed as:

$$\text{cathodic reaction:} \quad Li^+ + x/2O_2 + e^- \rightarrow LiO_x \qquad (2)$$

$$\text{anodic reaction:} \quad LiO_x \rightarrow Li^+ + x/2O_2 + e^- \qquad (3)$$

where O_2 denotes the unreacted oxygen in the reactant gas. Accordingly, a favourable species for the OCM reaction is generated in the neighbourhood of the electrode *via* both or either of the two reactions. However, the r/r_0 value of C_2-hydrocarbons decreased below 1 Hz. This will be explained later.

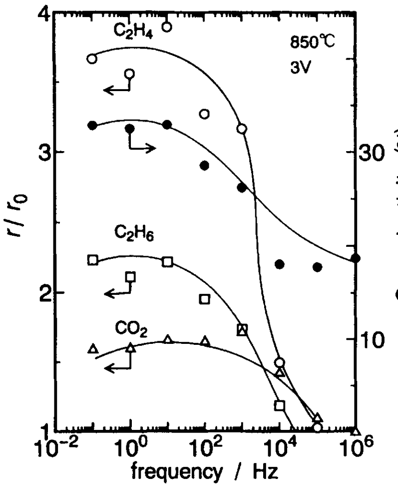

Fig. 4 Effect of frequency on formation rates of products and C_2-selectivity: reaction temperature 850 °C; ac voltage 3 V; experimental conditions as in Fig. 2

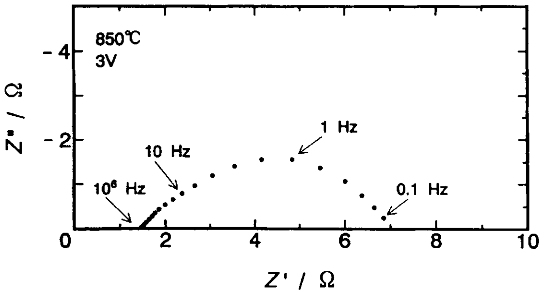

Fig. 5 Complex impedance plot of LBT membrane under the same experimental conditions as in Fig. 4

In order to clarify which of eqn. (2) and (3) improve the OCM reaction, we separated the cathodic and anodic reactions using a two-compartment cell [shown in Fig. 1(b)]. The experiment was carried out by applying a dc voltage of 2 V at 850 °C, where two mixtures of 8.3% CH_4 and 1.6% O_2 were fed into the two compartments. The results are summarized in Table 2. During the application of a dc voltage, the formation rates of C_2-hydrocarbons increased in the cathode compartment, but decreased in the anode compartment. This result indicates that eqn. (2) contributes to the generation of the favourable species for the OCM. However, compared to the application of an ac voltage, the r/r_0 value of C_2-hydrocarbons was less, and the r/r_0 value of CO_2 was larger. Consequently, Table 2 also suggests that the application of an ac voltage is preferable for the OCM reaction to the application of a dc voltage.

It has been established that the formation of a methyl radical from CH_4 is the rate-determining step for the OCM reaction. Over Li/MgO catalyst, Ito and Lunsford have proposed that the methyl radicals are formed as below[11]

$$Li^+O^- + CH_4 \rightarrow Li^+OH^- + CH_3^{\bullet} \qquad (4)$$

Many workers suggest that the active sites in this step are atomic O^- or diatomic $O^-{-}O^-$.[16–18] Similarly, it can be assumed that such oxygen species are effectively generated according to eqn. (2). This assumption is supported by the fact that when the reactant gas was free from O_2, the formation of C_2-hydrocarbons was little enhanced by applying an ac voltage to the LBT membrane. Consequently, we conclude that non-fully reduced oxide ions generated *via* the cathodic reaction abstract hydrogen from CH_4, forming methyl radicals.

The inferiority of dc electrolysis to ac electrolysis observed in Table 2 cannot be clearly explained from the above-mentioned results. However, the XRD measurement of the LBT membrane before and after the experiment showed that an unknown material was formed at the cathode as a result of the application of a dc voltage. It may be possible that this material is undesirable for the OCM reaction, so that the C_2-selectivity is significantly lowered. Similarly, this will be a reason for the decrease in r/r_0 value of C_2-hydrocarbons below 1 Hz shown in Fig. 4, because an ac voltage in such a frequency region is apparently regarded as a dc voltage.

Vayenas and co-workers have reported an NEMCA (Non-faraday electrochemical modification of catalytic activity) effect. Unfortunately, we cannot conclude whether the

Table 2 Oxidative coupling of CH_4 in the cathode and anode compartments

	open circuit						application of dc 2 V					
	formation rate /µmol min^{-1} cm^{-2}				conv. (%)	selec. (%)	formation rate /µmol min^{-1} cm^{-2}				conv. (%)	selec. (%)
	C_2H_4	C_2H_6	CO_2	CO	CH_4	C_2	C_2H_4	C_2H_6	CO_2	CO	CH_4	C_2
cathode	0.62	0.63	3.50	trace	3.53	26.2	0.67	0.64	4.20	trace	5.13	23.7
anode	0.62	0.63	3.50	trace	3.53	26.2	0.55	0.59	4.10	trace	3.74	21.6

Experimental conditions: temperature, 850 °C; reactant, 8.3% CH_4 + 1.6% O_2 (Ar balance) 24 cm^3 min^{-1}; dc voltage, 2 V.

observed behavior is such an effect or not, because we cannot exactly determine currents through the LBT membrane during the application of ac voltage. However, the r/r_0 value of C_2H_4 obtained in this study was of the order of 3 to 4, which is too small for the NEMCA process.

Conclusion

The LBT membrane offered the opportunity of an electrochemical enhancement for the OCM reaction. The application of an ac voltage to the LBT membrane specifically enhanced the formation of C_2-hydrocarbons. However, there was an appropriate range of temperature or frequency to observe this behaviour. It appeared that atomic O^- species were present in lithium oxide generated through the cathodic reaction and that this species served as an active site for the formation of C_2-hydrocarbons. The catalytic activity of such oxygen species was retained even at higher voltages.

References

1 G. E. Keller and M. M. Bhasin, *J. Catal.*, 1982, **73**, 9.
2 K. Otsuka, S. Yokoyama and A. Morikawa, *Chem. Lett.*, 1985, 319.
3 S. Seimanides and M. Stoukides, *J. Electrochem. Soc.*, 1986, **133**, 1535.
4 D. Eng and M. Stoukides, *Proceedings of the 9th International Congress on Catalysis*, Chemical Institute of Canada, Ottawa, 1988, vol. 2, p. 974.
5 B. C. H. Steele, I. Kelly, H. Middleton and R. Rudkin, *Solid State Ionics*, 1988, **28–30**, 1547.
6 N. U. Pujare and A. F. Sammells, *J. Electrochem. Soc.*, 1988, **135**, 2544.
7 K. Otsuka, K. Suga and I. Yamanaka, *Catal. Lett.*, 1988, **1**, 423.
8 P. H. Chiang, D. Eng and M. Stoukides, *J. Electrochem. Soc.*, 1991, **138**, L11.
9 L. S. Woldman and V. D. Sokolovskii, *Catal. Lett.*, 1991, **8**, 61.
10 T. Hibino, S. Hamakawa and H. Iwahara, *Chem. Lett.*, 1992, 1715.
11 T. Ito and J. H. Lunsford, *Nature (London)*, 1985, **314**, 721.
12 J. M. Deboy and R. F. Hicks, *J. Chem. Soc., Chem. Commun.*, **1988**, 982.
13 T. Hibino, A. Masegi and H. Iwahara, *J. Electrochem. Soc.*, 1995, **142**, 3262.
14 W. J. Zheng, R. Okuyama, T. Esaka and H. Iwahara, *Solid State Ionics*, 1989, **35**, 235.
15 T. Takahashi, H. Iwahara and T. Ichimura, *Denki Kagaku*, 1970, **38**, 852.
16 K. Otsuka, K. Jinno and A. Morikawa, *J. Catal.*, 1986, **100**, 1986.
17 J. S. Lee and S. T. Oyama, *Catal. Rev. Sci. Eng.*, 1988, **30**, 249.
18 J. A. Roos, S. J. Korf, R. H. J. Veehof, J. G. Van Ommen and J. R. H. Ross, *Appl. Catal.*, 1989, **52**, 131.

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