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AN EXPERIMENTAL STUDY OF OXIDATIVE COUPLING OF METHANE IN A SOLID OXIDE FUEL CELL WITH 1 wt%Sr/La_2O_3-Bi_2O_3-Ag-YSZ MEMBRANE

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Abstract – A solid oxide fuel cell with 1 wt%Sr/La_2O_3-Bi_2O_3-Ag-YSZ membrane was applied to oxidative coupling of methane. Membrane composition had a great effect on the reaction and current generated. An increase in the current generated was accompanied by a decrease in C_2 selectivity and an increase in CH_4 conversion. There is an optimal temperature for C_2-selectivity. CH_4 conversion decreased, C_2-selectivity increased and current generated decreased slightly with a rise in total flow rates. CH_4 conversion and the current generated increased with a rise in oxygen concentration. If only C_2-selectivity and current were concerned, the higher the methane concentration, the more favourable for the cogeneration of electrical energy and ethane and ethylene. Stability of the membrane was also tested.

Key words : Oxidative Coupling of Methane, Solid Fuel Cell, YSZ Membrane

INTRODUCTION

Methane is the major component of natural gas, a cheap, abundant natural resource. However, the primary use of methane is as fuel in which CO_2 and H_2O are combustion products. Oxidative coupling of methane (OCM) to produce ethane and ethylene has attracted much attention in recent years because of the increasing interest in the direct utilization of natural gas [Labinger, 1988]. Although a many studies have been conducted, the maximal yield of ethane and ethylene is just up to 25 % because the total oxidation of methane is thermodynamically favoured over the oxidative coupling of methane, and the products of ethane and ethylene tend to undergo further oxidation [Fox, 1993]. The oxidation coupling of methane has been studied mostly in conventional reactors. There are only a few studies which apply solid oxide fuel cells in the direct conversion of methane into useful chemicals. Pujare and Sammells [1987] studied the oxidative coupling of methane by using the cell Pt/Sm_2O_3/$La_{0.89}Sr_{0.10}MnO_3$/YSZ/$La_{0.89}Sr_{0.10}MnO_3$/Pt. YSZ stands for yttria stabilized zirconia, which is an oxygen ion conducting solid electrolyte and is widespread applied to fuel cells, oxygen pumps and oxygen sensors. High selectivity to C_2 hydrocarbon (>90 %) was obtained, but the methane conversion was low. Otsuka et al. [1990] also conducted an investigation in solid oxide fuel cells using YSZ as a solid electrolyte. In their experiment, catalysts such as KF, $BaCO_3$, NaCl/MnO_2, Sm_2O_3 deposited on Au-electrode were tested. They found that the most active and selective catalyst was $BaCO_3$ on Au. High selectivity was produced, but further studies were needed to stabilize the catalytic activity.

Previous study on oxidative coupling of methane over Bi_2O_3-Ag-YSZ membrane reactor [Otsuka et al., 1985] showed that methane oxidative dimerization could be promoted when only transported oxygen was available. 1 wt% Sr/La_2O_3 catalyst was one of the few catalysts capable of achieving C_2 selectivities ≥ 80 % at CH_4 conversions ≥ 15 % in a conventional reactor. The above observations encouraged us to combine 1 wt%Sr/La_2O_3 and Bi_2O_3-Ag as the catalyst-electrode to investigate the oxidative coupling of methane in a solid oxide fuel cell.

EXPERIMENTAL

1. Preparation of Electrodes

The model solid oxide fuel cells used in this study were prepared from tubes of 8 mol% yttria stabilized zirconia (YSZ) with dimension 9 mm ID × 11 mm OD × 150 mm long. The YSZ tubes were prepared from powders by type casting. Ag electrodes were coated on the central section of the inside and outside tube surfaces with 50 mm length, respectively. The electrodes were made by the following procedure. First, the YSZ tube was cleaned by rinsing in an ultrasonic bath, followed by drying and calcining for 4 h at 1,223 K. After the YSZ tube was cooled down naturally, it was slightly heated and coated by a suspension of nitro-cellulose/butyl acetate of $AgNO_3$ with appropriate composition onto both the outside and inside surface of the YSZ tube, followed by drying and calcining at 953 K. The procedure was repeated several times in order to achieve an electrode resistance of less than 0.30 Ω.

2. Preparation of Catalyst Layer

The catalyst layer consisted of 1 wt%Sr/La_2O_3-Bi_2O_3, made from $Sr(NO_3)_2$, La_2O_3, $Bi(NO_3)_3 \cdot 5H_2O$. Bi_2O_3 catalyst was prepared by calcining $Bi(NO_3)_3 \cdot 5H_2O$ at 873 K for 2 h and grinding Bi_2O_3 to fine powder. 1 wt%Sr/La_2O_3 catalyst was pre-

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pared by incipient wetness impregnation, dried for 12 h at 383 K, and calcined for 6 h at 1,073 K, and then ground to fine powder. Bi_2O_3 and 1 wt%Sr/La_2O_3 were coated in a suspension of the nitro-cellulose/butyl acetate onto the outside of Ag-YSZ tube, followed by drying and calcining in air.

3. Cell Design

A diagram of the configuration of the cell is in Fig. 1. The membrane tube was fitted into a quartz tube with 22 mm ID to form a shell and tube heat exchanger arrangement. Ag wire was attached to the YSZ tube to carry current to the external circuit.

4. Apparatus

The cell was placed into a tubular furnace and a EUROTHERM808 temperature controller was used to control the temperature within ±2 K. Electrical measurements were made by two HP 34401A multimeters. All data were collected by placing a variable load across the cell. During tests, the anode chamber was flushed with N_2 before the fuel was introduced. The fuel of the mixture of CH_4 and N_2 was put into the shell side at a total flow rate of 3.41×10^{-5} mol/s. Air used as oxygen source was put into the tube side of the cell at a flow rate 1.705×10^{-5} mol/s. Flow rates were measured by mass flow controllers. Gas compositions were analyzed by an HP on-line gas chromatograph with a thermal conductivity detector. Two columns packed with Porapak Q and molecular sieve 5A was used. The main detectable products were C_2H_6, C_2H_4, CO_2, H_2, H_2O. There were negligible amounts of CO in the products. Carbon atom balance did not exceed ±2%. However, water was not quantitatively analyzed in all experiments.

CH_4 conversion and C_2 selectivity are calculated by:

$$X_{CH4}=(F^0_{CH4}-F_{CH4})/F^0_{CH4} \tag{1}$$

$$Sc_2=2(F_{C2H4}+F_{C2H6})/(F^0_{CH4}-F_{CH4}) \tag{2}$$

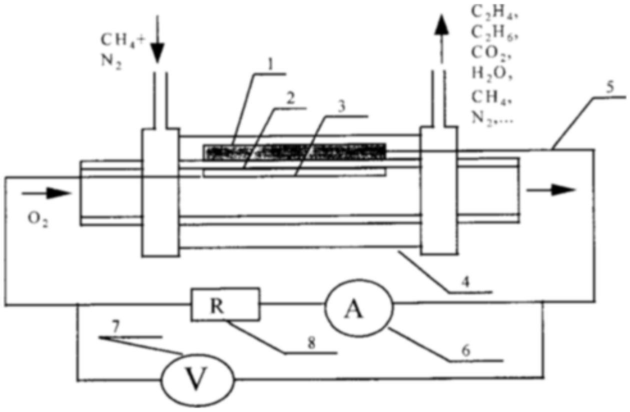

Fig. 1. The configuration of solid oxide fuel cell 1-catalyst/electrode (1 wt%Sr/La_2O_3-Bi_2O_3-Ag); 2-YSZ tube; 3-electrode (Ag); 4-quartz tube; 5-Ag wire; 6-multimeter used as galvanometer; 7-multimeter used as voltmeter; 8-resistance box.

RESULTS AND DISCUSSION

1. Effect of Membrane Composition

In order to investigate the effect of composition of membrane on the performance of the reaction, the Ag-YSZ, 1 wt% Sr/La_2O_3-Ag-YSZ, 1 wt%Sr/La_2O_3-Bi_2O_3-Ag-YSZ membranes were tested in the solid oxide fuel cells for OCM reaction. Table 1 summarizes the results obtained under the same operation conditions as in the footnote to the table. Compared with the results for the Ag electrode alone, C_2 selectivity was improved greatly from 41.3% for Ag to 90.2% for 1 wt% Sr/La_2O_3-Bi_2O_3-Ag-YSZ, C_2 yield ranged from 0.66% for Ag to 0.98% for 1 wt%Sr/La_2O_3-Bi_2O_3-Ag-YSZ. This demonstrated that the composition of electrode-catalyst affected the reaction dramatically. Among the membranes tested, 1 wt% Sr/La_2O_3-Bi_2O_3-Ag-YSZ showed the highest C_2 selectivity and yield and the second largest current. Therefore, the following experiments were carried out in the solid oxide fuel cell with 1 wt% Sr/La_2O_3-Bi_2O_3-Ag-YSZ membrane.

2. Effects of Operation Conditions

A typical current-potential plot at constant feed composition is given in Fig. 2. The cell voltage attained under open circuit was up to 0.76 V and decreased quasi-linearly with increasing current. This indicated that at the range of the temperatures ohmic overpotential was the dominant source of polarization. Therefore, the performance of the solid oxide fuel cell could be improved significantly by appropriate decrease of the electrolyte resistance. The power as a function of current is also displayed in Fig. 2. The maximum power generation was about 7 mW. Fig. 3 shows the dependence

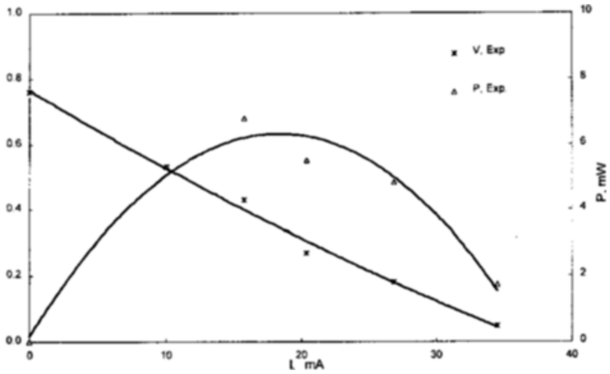

Fig. 2. Voltage-current and power-current (T=1,003.15 K, anode: $F_t=3.41\times10^{-5}$ mol/s, P_{CH4}=20.3 kPa, cathode: $Q_t=1.705\times10^{-4}$ mol/s, P_{O2}=21.3 kPa)

Table 1. Oxidative coupling of methane in the solid oxide fuel cell with different membranes

Membrane	CH_4 conversion, %	C_2 selectivity, %	C_2 yield, %	Current mA
Ag-YSZ	1.6	41.3	0.66	37.2
1 wt%Sr/La_2O_3-Ag-YSZ	1.2	80.4	0.96	29.6
1 wt%Sr/La_2O_3-Bi_2O_3-Ag-YSZ	1.09	90.2	0.98	34.5

Reaction conditions: T=1,003 K, R=0.1 Ω, anode: $F_t=3.41\times10^{-5}$ mol/s, P_{CH4}=20.3 kPa, cathode: $Q_t=1.705\times10^{-4}$ mol/s, P_{O2}=21.3 kPa)

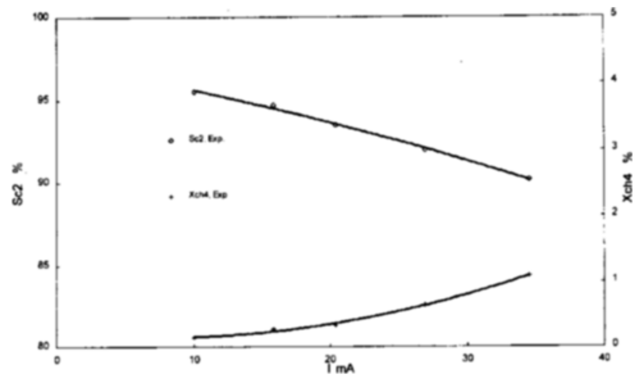

Fig. 3. C_2 selectivity and CH_4 conversion versus current (T=1,003.15 K, anode: F_t=3.41×10^{-5} mol/s, P_{CH4}=20.3 kPa, cathode: Q_t=1.705×10^{-4} mol/s, P_{O2}=21.3 kPa).

of CH_4 conversion and C_2 selectivity on current. An increasing current was accompanied by a decrease in C_2 selectivity and an increase in CH_4 conversion.

The dependence of C_2 selectivity, CH_4 conversion and current on temperature at constant feed composition and the total flow rate is shown in Figs. 4 and 5. It was observed that the C_2-selectivity initially increased with a rise in temperature and then decreased. The optimum temperature for the synthesis of C_2 hydrocarbons was about 1,023 K. The CH_4 conversion showed an increase with increasing temperature. The current generated increased with a rise in temperature as expected. This was due to the fact that, in general, the ionic conductivity increased exponentially with temperature following approximately an Arrhenius expression. It was generally accepted that the $CH_3\cdot$ radicals were generated on the surface of catalyst, and two $CH_3\cdot$ radicals were combined primarily in the gas phase to form C_2H_6. C_2H_6 could be further oxidized or dehydrogenated to C_2H_4. C_2H_6 and C_2H_4 also reacted with oxygen to form CO_2 and H_2O. Under high temperatures, many more C_2 hydrocarbons were further oxidized, leading to a drop in C_2 selectivity. Fig. 6 shows the effect of temperature on the alkene to alkane ratio. The alkene to alkane ratio increases with a rise in temperature. It was demonstrated that C_2H_4 was formed from C_2H_6 as a secondary product.

The dependence of C_2-selectivity and CH_4 conversion and current generated on methane concentration is shown in Figs. 7 and 8. N_2 was used as a diluent. With increasing CH_4 concentration in the feed stream, C_2-selectivity increased, CH_4 conversion decreased and the current generated increased quasi-linearly. If only C_2-selectivity and current were concerned, the higher the methane concentration, the more favourable

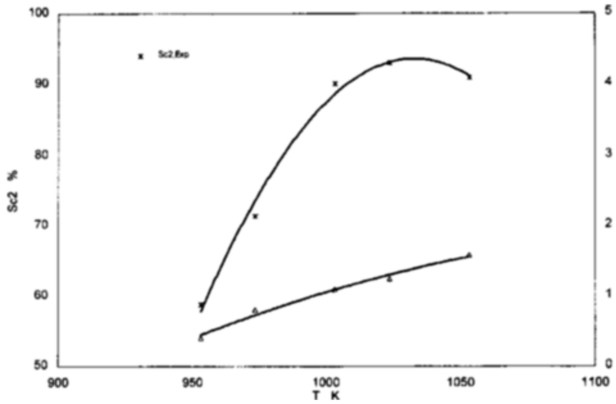

Fig. 4. C_2 selectivity and CH_4 conversion as a function of temperature (R=0.1 Ω, anode: F_t=3.41×10^{-5} mol/s, P_{CH4}=20.3 kPa, cathode: Q_t=1.705×10^{-4} mol/s, P_{O2}=21.3 kPa).

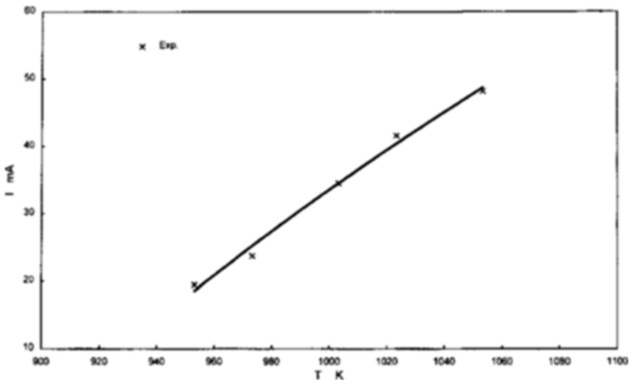

Fig. 5. Current as a function of temperature (reaction conditions are the same as those of Fig. 4).

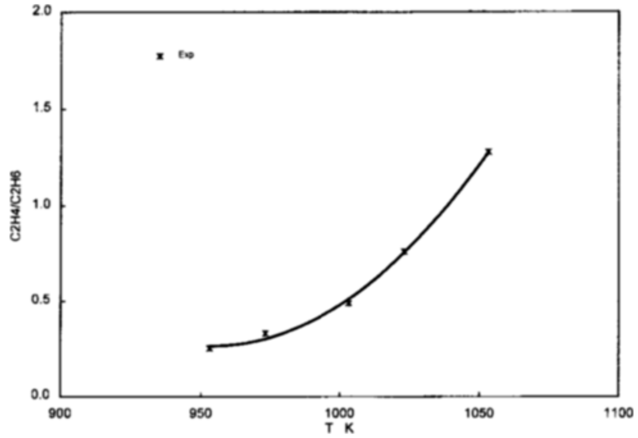

Fig. 6. C_2H_4/C_2H_6 as a function of temperature (reaction conditions are the same as those of Fig. 4).

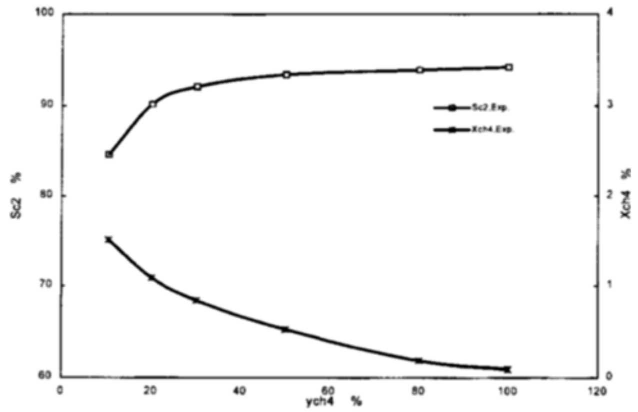

Fig. 7. C_2 selectivity and CH_4 conversion as a function of feed methane mole fraction (T=1,003.15 K, R=0.1 Ω, anode: F_t=3.41×10^{-5} mol/s, cathode: Q_t=1.705×10^{-4} mol/s, P_{O2}=21.3 kPa).

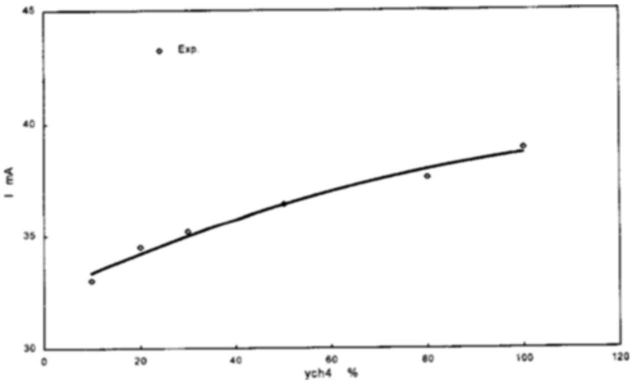

Fig. 8. Current as a function of feed methane mole fraction (reaction conditions are the same as those of Fig. 7).

for cogeneration of electrical energy and ethane and ethlyene. No O_2 was detected in the GC analysis; thus oxygen conversion was about 100 % in the experiments. The amount of oxygen limited the reaction.

Figs. 9 and 10 show the effect of oxygen concentration in the cathode chamber on the cogeneration. CH_4 conversion and the current generated increased with a rise in oxygen concentration. There was no obvious influence of oxygen concentration on C_2-selectivity. The driving force of the solid oxide fuel cell is the gradient of chemical potentials between the anode and the cathode. The difference of the oxygen concentration between the anode and cathode increased with a rise in oxygen concentration in the cathode chamber.

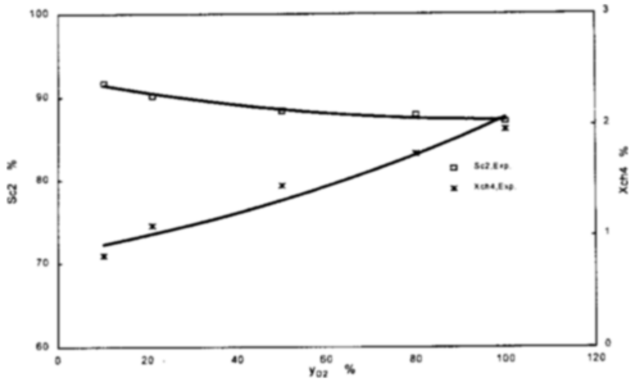

Fig. 9. C_2 selectivity and CH_4 conversion as a function of oxygen mole fraction in the cathode chamber (T=1,003.15 K, R=0.1 Ω, anode: F_t=3.41×10^{-5} mol/s, P_{CH4}=20.3 kPa, cathode: Q_t=1.705×10^{-4} mol/s).

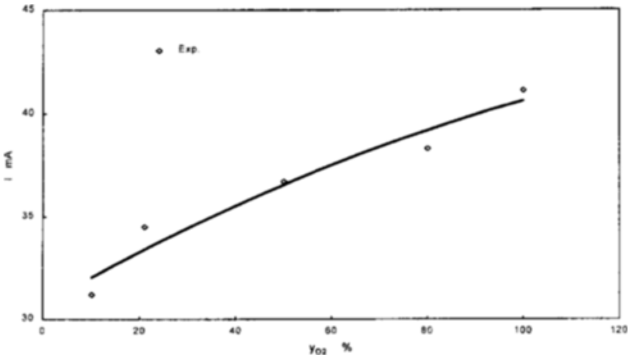

Fig. 10. Current as a function of oxygen mole fraction in the cathode chamber (reaction conditions are the same as those of Fig. 9).

Figs. 11 and 12 show the effect of total flow rates in the anode chamber on the performance of the solid oxide fuel cell. Over the eight-fold variation in the flow rate, CH_4 conversion decreased, C_2-selectivity slightly increased and current generated decreased slightly with a rise in total flow rates. However, the alkene to alkane ratio increased obviously with a rise in total flow rates. Under constant feed composition, temperature, the flow rate of methane increased with an increase in total flow rates, leading to a decline in the ratio of methane to oxygen; therefore C_2-selectivity increased. However, the current generated was low; thus the total flow rate did not influence the C_2-selectivity greatly when the total flow rate was greater than 200 ml/min.

3. Stability of the Membrane

The stability of the membrane is illustrated in Fig. 13. The membrane was tested for 62 h with no significant loss of activity. C_2-selectivity and CH_4 conversion remained relatively constant with increasing reaction time.

CONCLUSION

Oxidative coupling of methane was studied in a solid ox-

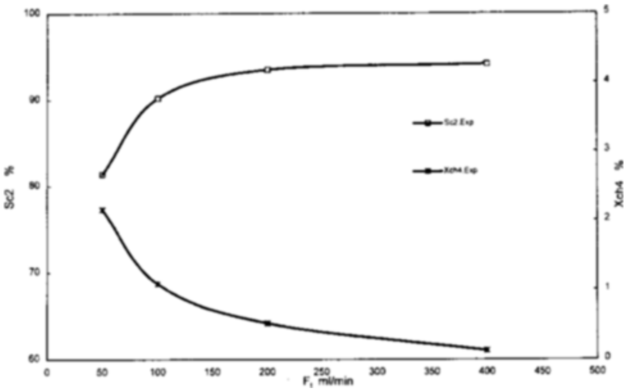

Fig. 11. C_2 selectivity and CH_4 conversion as a function of flow rate (T=1,003.15 K, R=0.1 Ω, anode: P_{CH4}=20.3 kPa, cathode: Q_t=1.705×10^{-4} mol/s, P_{O2}=21.3 kPa).

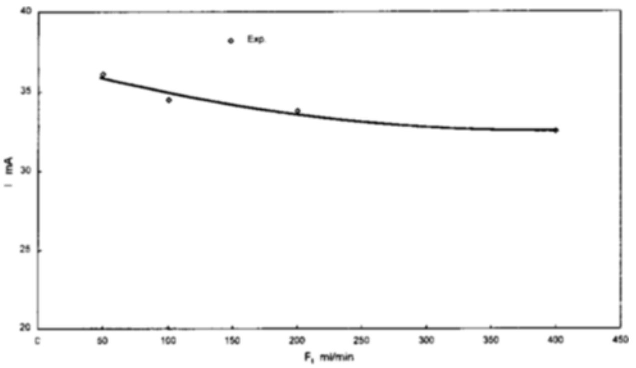

Fig. 12. Current as a function of the flow rate (reaction conditions are the same as those of Fig. 11).

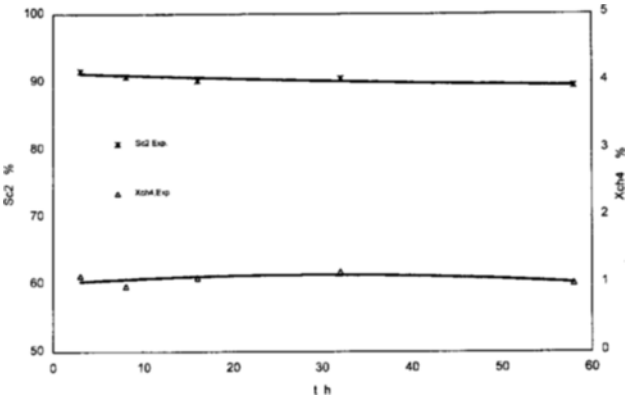

Fig. 13. C_2 selectivity and CH_4 conversion versus reaction time (T=1,003.15 K, R=0.1 Ω, anode: F_t=3.41×10^{-5} mol/s, P_{CH4}=20.3 kPa, cathode: Q_t=1.705×10^{-4} mol/s, P_{O2}=21.3 kPa).

ide fuel cell with 1 wt%Sr/La_2O_3-Bi_2O_3-Ag-YSZ membrane with simultaneous generation of electrical energy. The C_2 product selectivity, CH_4 conversion and current generated were a function of temperature, total flow rate, feed composition. In the present experiments, the dominant source of polarization was ohmic. The fuel cell was operated successfully for an extended period of time.

NOMENCLATURE

F_i : mole flow rate [mol/s]
F_t : total flow rate in the anodic compartment [mol/s]
I : current [A]
P_i : i component partial pressure [Pa]
Q_t : total flow rate in the cathodic compartment [mol/s]
R : resistance [Ω]
Sc_2 : C_2-selectivity [%]
T : temperature [C]
V : voltage [V]
P : power [W]
X_{CH4} : CH_4 conversion [%]
y_{CH4} : CH_4 mole fraction [%]
y_{O2} : O_2 mole fraction [%]

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