CHAPTER V

RESULTS AND DISCUSSION

5.1 Preliminary Selection of Anode Catalyst

The methane pulse reaction technique was employed for preliminary selection of the anode catalyst for the SOFC reactor because oxygen provided to the reaction was quite similar to oxygen supplied from the cathode side via an electrolyte to the anode in the SOFC reactor. This method is much cheaper than direct operation with a complete cell assembly in the SOFC reactor, which requires an expensive YSZ electrolyte for each run and involves rather complicated procedures, especially at the cell assembly step. However, the error in calculation depends largely on time and number of samples taken.

Figure 5.1 shows the effect of Al content (x=0, 0.2, 0.3, 0.5, 0.8 and 1.0) of the anode catalyst, $Sm_{2-x}Al_xO_3$, on methane conversion and C_2 hydrocarbons selectivity. It was found that the methane conversion increases and the C_2 selectivity decreases with the increasing amount of Al in the catalyst. Thus, a maximum yield of about 5% is observed at x=0.5. It should be noted that when the Al content is higher than 0.5, the C_2 selectivity decreases sharply. Consequently, only the anode catalysts with x=0, 0.2, 0.3 and 0.5 were selected for further study in the SOFC reactor.
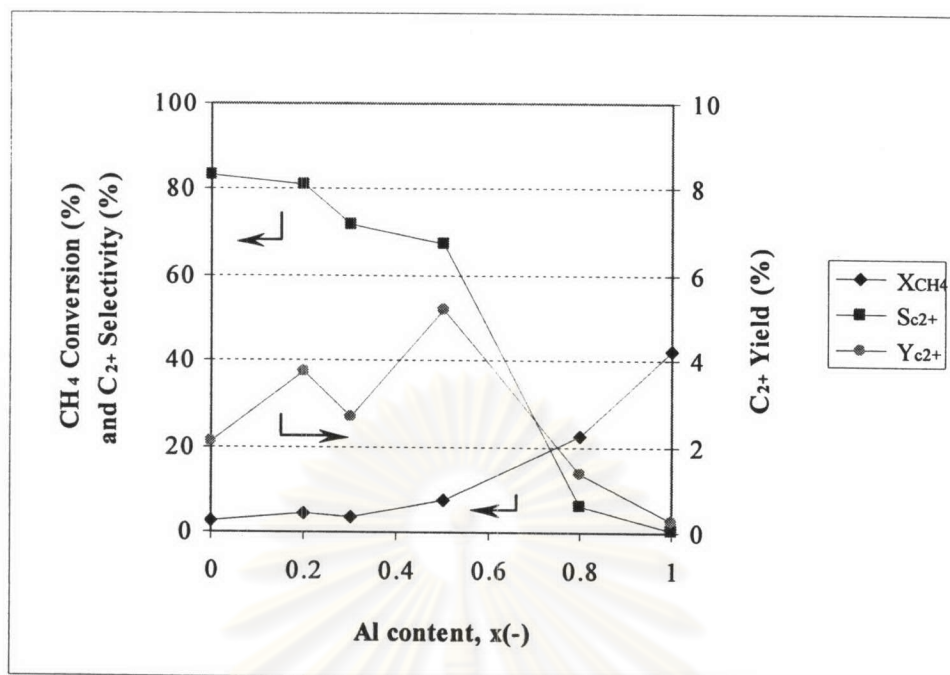
Figure 5.1 Results of Catalytic Performance of the SmAlO Catalysts from the Methane Pulse Reaction Method

5.2 Anode Catalyst Characterization

The anode catalysts (x = 0, 0.2, 0.3 and 0.5) in powder form were characterized to find their specific surface area (BET), x-ray diffraction (XRD) pattern and electrical conductivity.

The values of the surface area of the catalysts pretreated at T = 1173 K in air for 3 hr is summarized in Table 5.1. The surface area of the Sm_2O_3 catalyst increases with the increasing Al content in the catalyst.

Table 5.1 Surface Area of Anode Catalysts

Catalyst	Sm_2O_3	$Sm_{1.8}Al_{0.2}O_3$	$Sm_{1.7}Al_{0.3}O_3$	$Sm_{1.5}Al_{0.5}O_3$
Surface area (m^2/g)	2.9	4.0	4.2	4.7

The XRD patterns of the selected catalyst are shown in Figure 5.2. When Al is added to the Sm_2O_3 catalyst, the $2Sm_2O_3Al_2O_3$ structure is formed. The $SmAlO_3$ phase is only found for the $Sm_{1.5}Al_{0.5}O_3$ catalyst as shown in Figure 5.2. For all compositions of the SmAlO catalysts, the Sm forms compounds with Al and the Al_2O_3 phase is not detected.
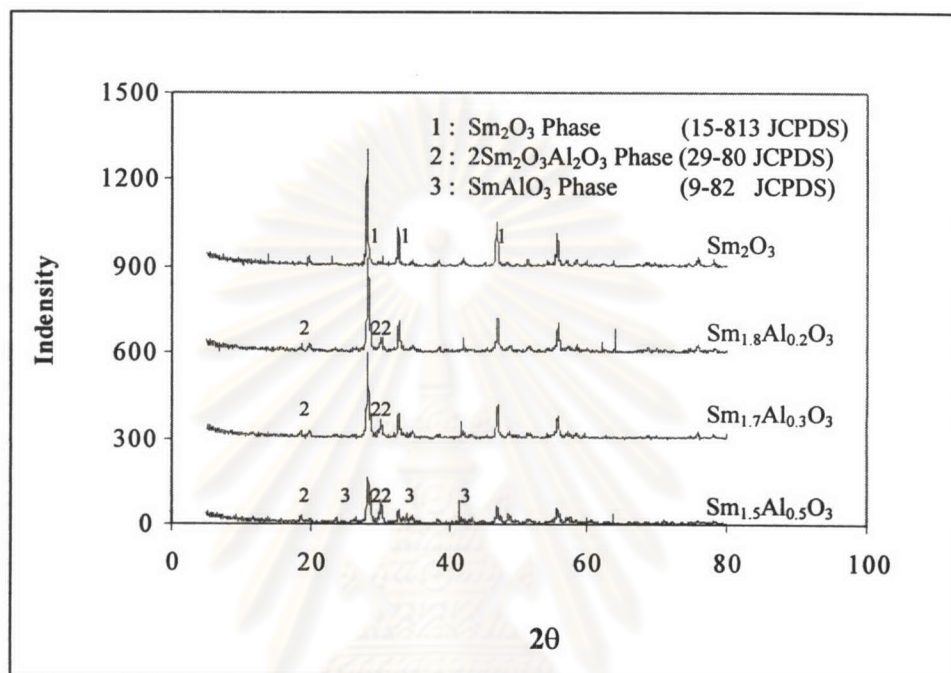
Figure 5.2 X-ray Diffraction Patterns for SmAlO Catalyst

The electrical conductivity of the anode catalysts was measured at temperature between 1023 and 1273 K under two different oxygen contents (21% and 1%). The results are shown in Figures 5.3 and 5.4. It was found that the electrical conductivity of all the catalysts at the oxygen content of 21% is higher than that of 1% all over the temperature ranges. From these results, the catalysts should show p-type conductive characteristic. For p-type conductor, the charge carriers are positive holes which can be originated from chemisorption of gaseous oxygen on the catalyst (on oxygen vacancy) or from the incorporation of gaseous oxygen into the crystal lattice (Dubois and Cameron, 1990; Filkova *et al.*, 1997). Consequently, when the oxygen concentration in the gas phase is higher, the electrical conductivity for the p-type conductor is higher.

Considering the effect of addition of Al in the catalyst, it was found that increasing the Al content decreases the conductivity of the Sm_2O_3 as shown in Figures 5.3 and 5.4. This can be explained that the lower electropositive character (weaker electronegative) of Al than that of Sm makes the probability of finding oxygen vacancies or inserted oxygens decreased due to its ability of donating electrons to form oxygen vacancies or inserted oxygens. Therefore, the higher Al content results in the lower p-type conductivity. It should be noted that according to the relationship between conductivity and chemisorption of oxygen gas above, the basicity of the catalyst increases with the increased p-type conductive ability (Dubois and Cameron, 1990). Consequently, the addition of Al should decreases the basicity of the catalyst because the lower electropositivity of Al shows the lower basicity than Sm.
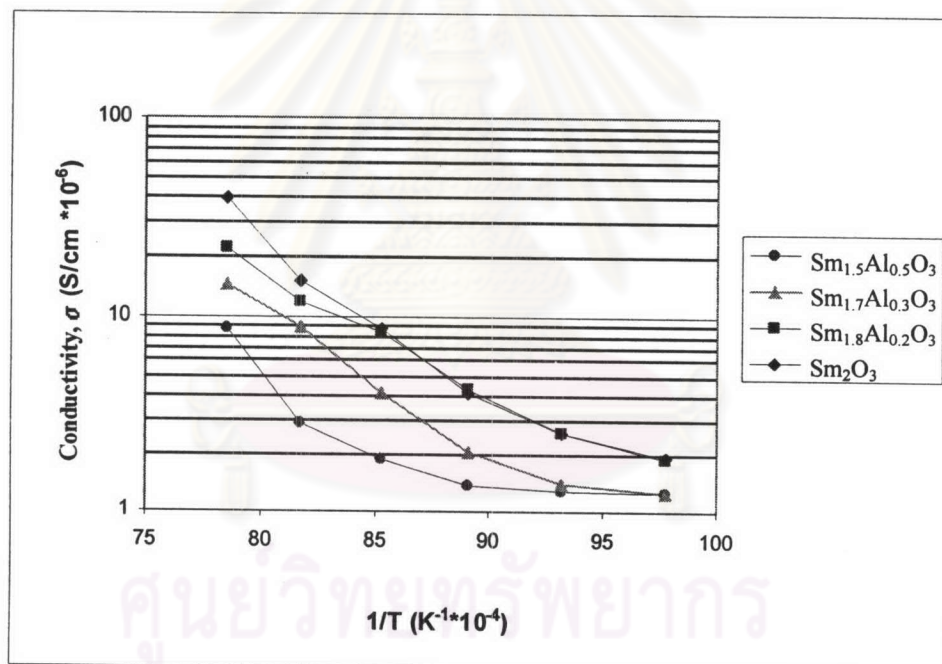

Figure 5.3 Electrical Conductivity of Anode Catalysts in Air ($O_2 = 21\%$)

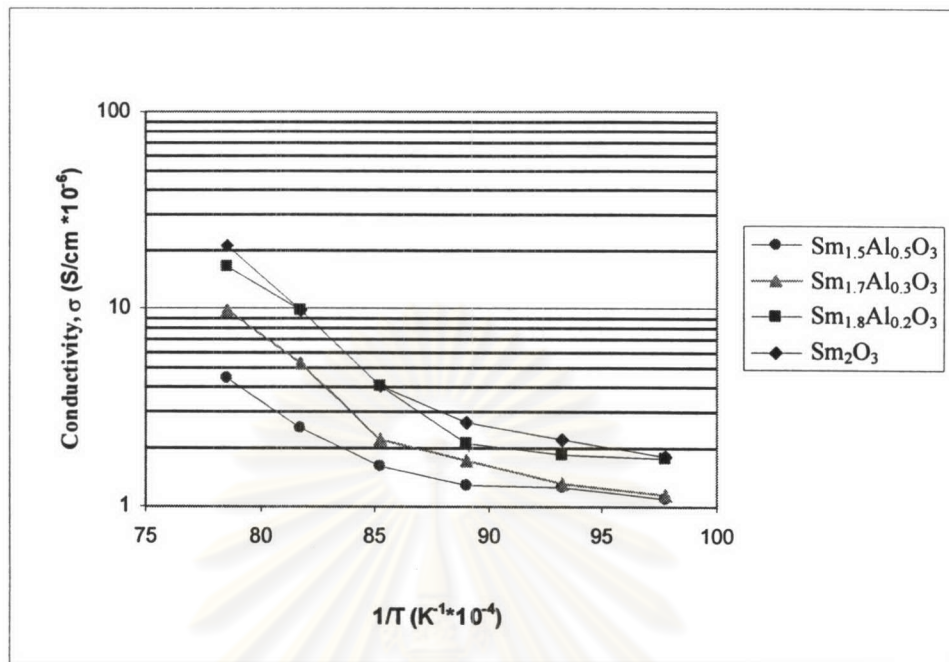**Figure 5.4** Electrical Conductivity of Anode Catalysts under 1% O_2

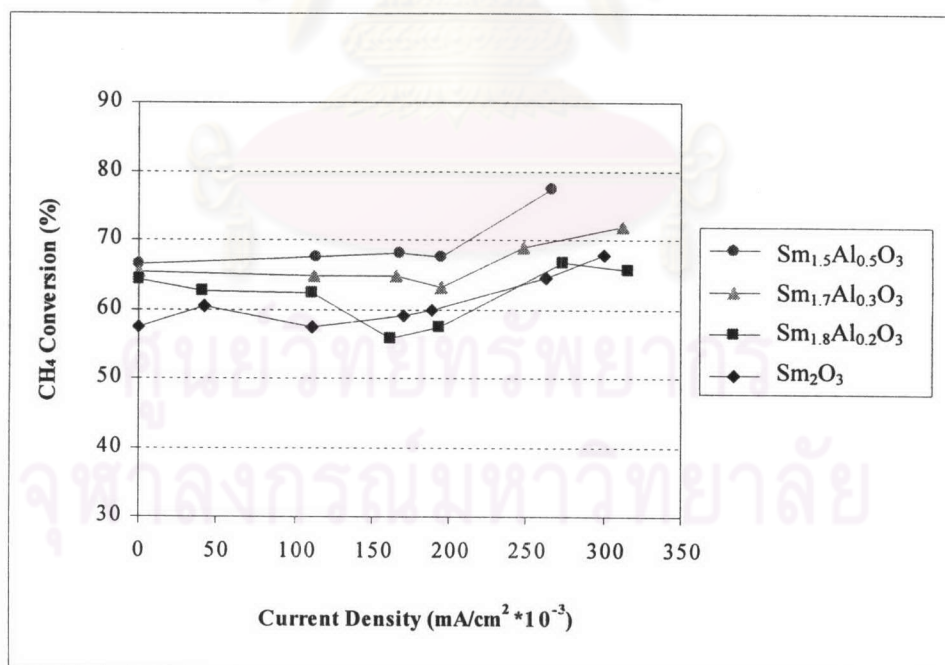## 5.3 Effect of Metal Composition of Anode Catalyst

The results of the effect of the anode metal composition on the methane conversion, C_{2+} selectivity and C_{2+} yield under various current density at $T= 1173$ and 1273 K are shown in Figures 5.4 (a)-(f).
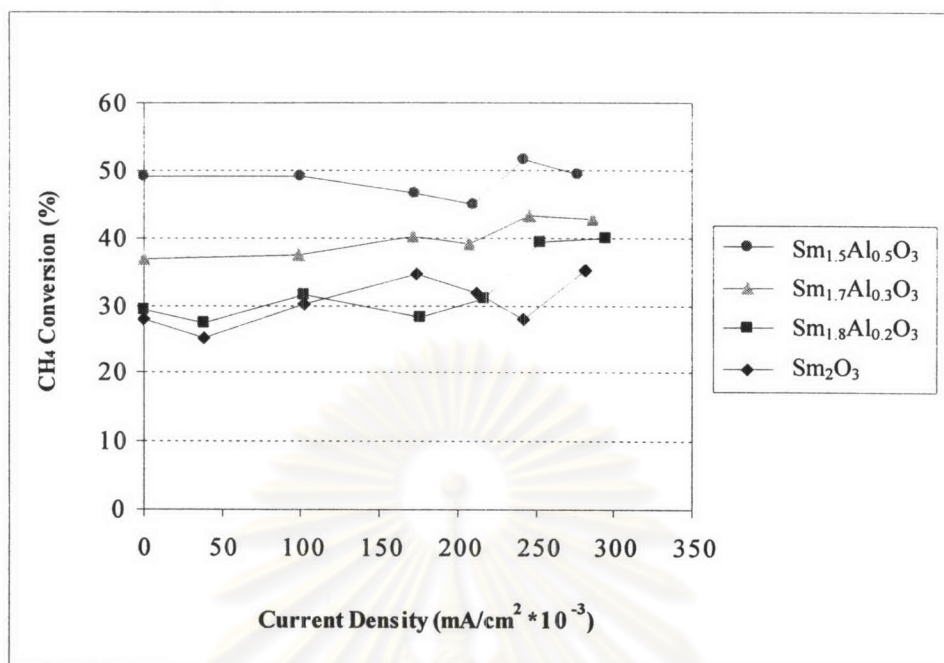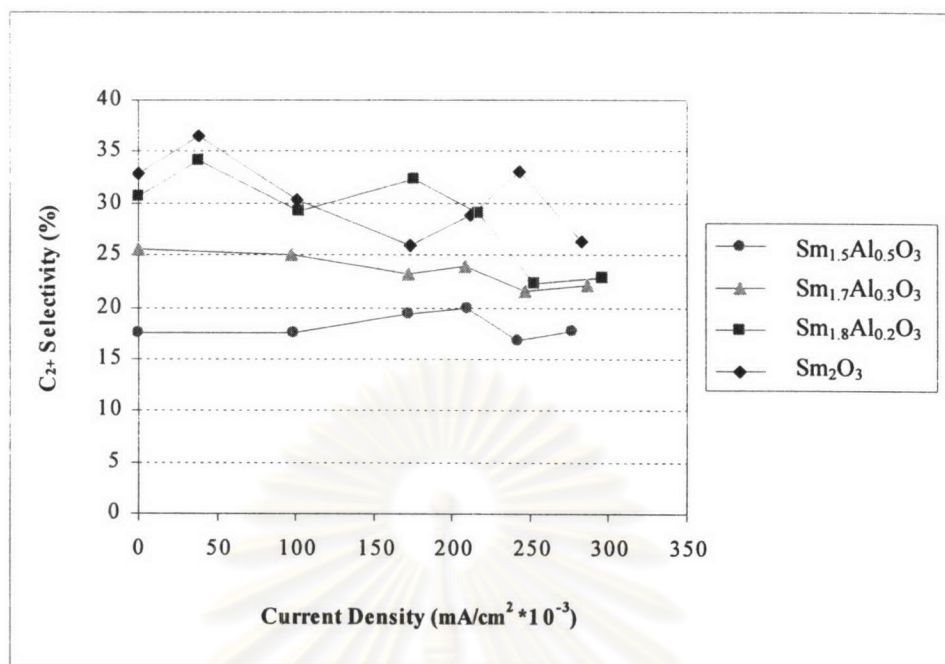
(a) at 1173 K

(b) at 1273 K

(c) at 1173 K

(d) at 1273 K

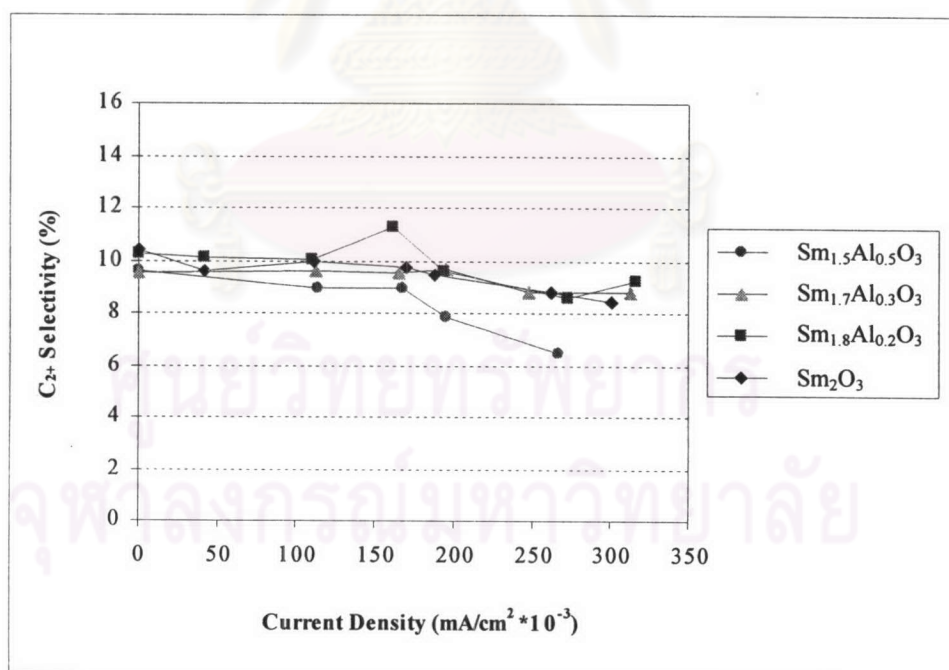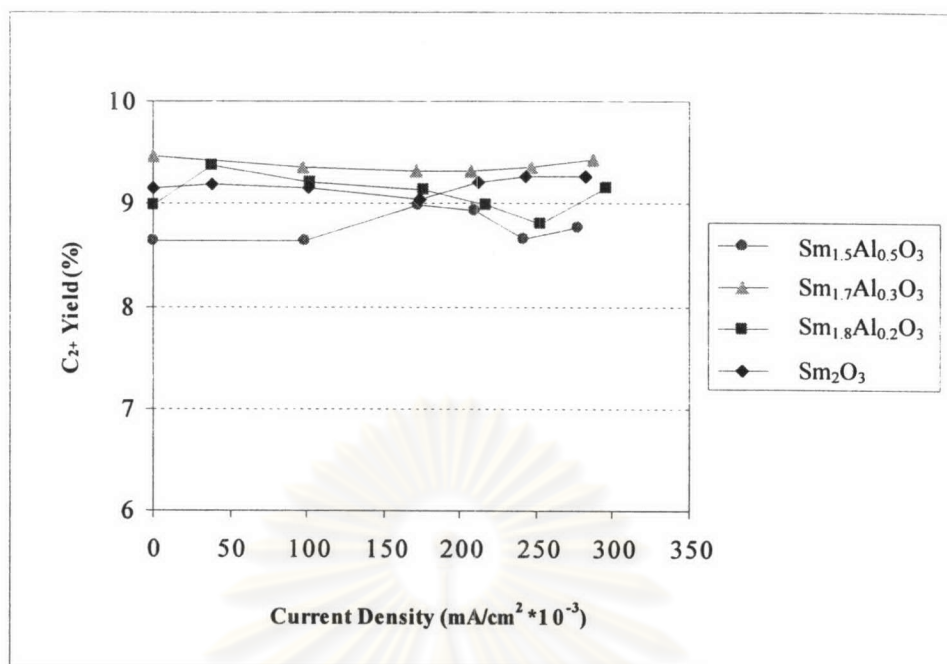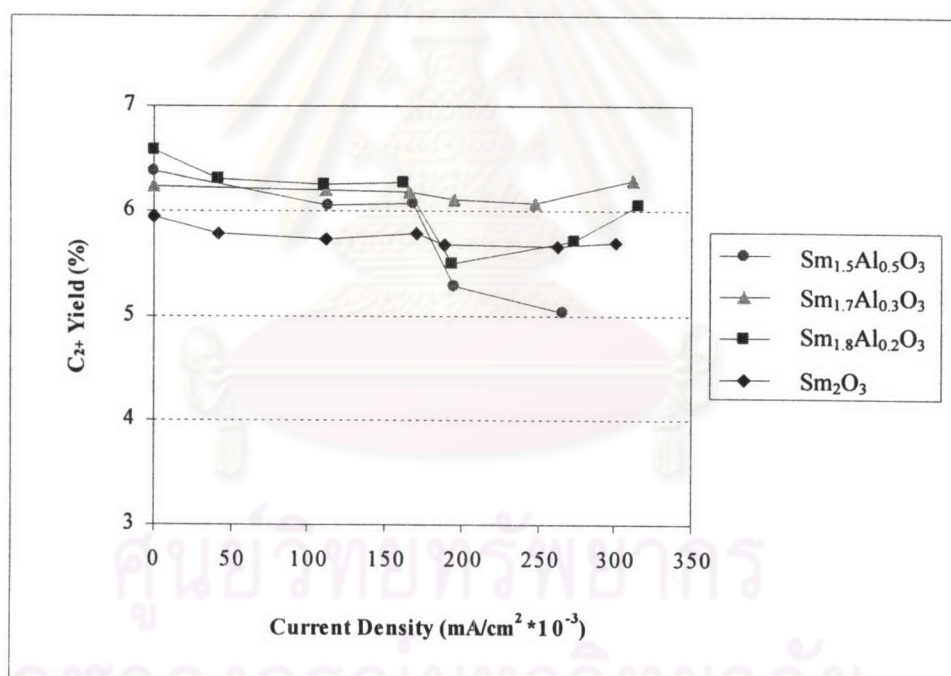(e) at 1173 K

(f) at 1273 K

Figure 5.5 Effect of Metal Composition on Catalytic Performance: CH_4 Conversion at 1173 K (a) and 1273 K (b), C_{2+} Selectivity at 1173 K (c) and 1273 K (d), and C_{2+} Yield at 1173 K (e) and 1273 K (f).

Table 5.2 Results of Effect of Metal Composition on Catalytic Performance at T=1173 K

Catalyst	Current density	E	Power density	CH_4 Conversion	Selectivity				C_{2+} Yield
					C_{2+}	CO_2	CO	C balance	
	$mA/cm^2 \cdot 10^{-3}$	mV	$mW/cm^2 \cdot 10^{-3}$	%	%	%	%	%	%
Sm_2O_3	0	855	0	28	33	3.4	5.0	59	9.1
	102	824	84	30	30	0.8	2.3	67	9.1
	174	815	141	35	26	2.1	1.8	70	9.0
	212	813	172	32	29	1.2	2.6	67	9.2
	282	813	229	35	26	4.5	0.9	68	9.3
$Sm_{1.8}Al_{0.2}O_3$	0	850	0	29	31	2.3	5.6	61	9.0
	102	829	84	32	29	1.4	5.0	64	9.2
	176	828	146	28	32	2.6	5.3	60	9.1
	216	831	180	31	29	3.2	4.8	63	9.0
	295	833	251	40	23	1.6	3.9	72	9.2
$Sm_{1.7}Al_{0.3}O_3$	0	813	0	37	26	1.1	6.9	66	9.5
	98	806	79	38	25	2.0	6.8	66	9.4
	172	808	139	40	23	2.2	6.4	68	9.3
	208	817	170	39	24	2.5	6.6	67	9.3
	287	827	237	43	22	2.2	6.0	70	9.4
$Sm_{1.5}Al_{0.5}O_3$	0	840	0	49	18	2.2	10.0	70	8.6
	99	806	80	49	18	2.5	11.5	68	8.6
	172	803	138	47	19	2.9	11.2	67	9.0
	277	798	221	49	18	2.7	11.1	68	8.8
Empty Quartz	-	-	-	33	14	1.52	N/D	85	4.5
$La_{1.8}Al_{0.2}O_3$	0	973	0	45	20	1.8	15.2	63	9.2
	31	958	30	49	17	0.8	14.7	68	8.3
	81	921	74	72	12	0.5	10.7	77	8.4
	135	893	121	56	15	0.9	12.5	72	8.1

Table 5.3 Results of Effect of Metal Composition on Catalytic Performance at T=1273 K

Catalyst	Current density	E	Power density	CH_4 Conversion	Selectivity				C_{2+} Yield
					C_{2+}	CO_2	CO	C balance	
	mA/cm^2*10^{-3}	mV	mW/cm^2*10^{-3}	%	%	%	%	%	%
Sm_2O_3	0	922	0	57	10	2.2	14	73	6.0
	111	909	101	57	10	0.8	15	74	5.7
	170	895	152	59	10	2.7	14	73	5.8
	262	873	229	65	9	3.1	14	74	5.7
	301	866	261	68	8	0.6	13	78	5.7
$Sm_{1.8}Al_{0.2}O_3$	0	905	0	64	10	0.3	12	78	6.6
	111	903	100	62	10	0.7	12	77	6.3
	162	902	146	56	11	1.0	13	75	6.3
	274	911	249	67	9	0.4	13	78	5.7
	316	914	289	66	9	0.4	13	77	6.1
$Sm_{1.7}Al_{0.3}O_3$	0	930	0	65	10	2.3	10	78	6.2
	112	924	104	65	10	2.4	12	76	6.2
	166	922	153	65	10	2.3	12	76	6.2
	248	910	226	69	9	2.2	11	78	6.1
	312	900	281	72	9	2.2	12	77	6.3
$Sm_{1.5}Al_{0.5}O_3$	0	948	0	67	10	0.8	14	75	6.4
	113	923	105	68	9	2.5	11	77	6.1
	168	920	155	68	9				6.1
	267	914	244	77	7	2.0	12	79	5.0
	325	911	296						
Empty Quartz	-	-	-	49	9	0.76	N/D	91	4.2
$La_{1.8}Al_{0.2}O_3$	0	957	0	69	12	0.5	14.5	74	7.9
	20	951	19	75	11	1.9	7.3	80	7.9
	141	932	131	78	11	2.0	14.8	73	8.2
	222	896	199	57	15	2.4	23.6	59	8.5

According to the experimental results in Fig 5.5 and Tables 5.2 and 5.3, it was found that the OCM and the incomplete combustion are the major reactions taken place in the SOFC reactor. The selectivity of the valuable chemicals (CO and C_{2+}) was much higher than that of CO_2. This result agrees well the result of $La_{1.8}Al_{0.2}O_3$ catalyst in the previous work (Tagawa *et al.*, 1999). In addition, comparing to the catalyst in literature that shows the good yield, $La_{1.8}Al_{0.2}O_3$, the SmAlO catalysts except $Sm_{1.5}Al_{0.5}O_3$ show more C_{2+} yield at 1173 K but less at 1273K. It should be noted that preliminary tests at $T = 1073$ K show low performance. This should be due to low catalytic activity. As a result, they are not considered in the thesis.

From Figure 5.5, at 1173 K and over all the range of current densities, the increase in the Al content resulted in the increase in the methane conversion and the decrease in the C_{2+} selectivity. However, the carbon decomposition compound was likely unchanged. At 1273 K, the trends were similar to those of at 1173 K but the difference was not pronounced.

Considering the carbon decomposition compound that is indicated by the terms of carbon balance in Table 5.2 and 5.3, it was found that the decomposition was large in all SmAlO catalysts. However, from the experiment using empty quartz with an YSZ electrolyte and without anode catalyst at same operating conditions, the carbon decomposition compound was occurred on the o-ring and quartz tube surface and its selectivity was about 90% at T=1173 and 1273 K. Therefore, the main carbon decomposition compound occurred in each run could be accounted from the unreacted methane that was converted to carbon compound.

It was found that at the same current density or the same oxygen flux, the methane conversion at 1273 K was higher than that at 1173 K. The formation of carbon monoxide requires oxygen consumption around three times higher than the formation of C_{2+} hydrocarbon ($CH_4+1.5O_2 = CO+2H_2O$ and $CH_4+0.5O_2 = 0.5C_2H_4+H_2O$). Hence, the selectivity of carbon monoxide should be lower while the selectivity of C_{2+} hydrocarbon should be higher at 1273 K than at 1173. However, this is not consistent with the experimental results. It may be because at high temperature and with the presence of steam obtained from the electrochemical reactions, methane can be reformed to carbon monoxide and hydrogen by the steam reforming reaction whose reaction rate becomes faster at higher temperature. In addition, methane can be easily decomposed to carbon compounds on the catalyst surface at high temperature.

When the current density or the oxygen supply rate increases, the methane conversion should increase while the C_{2+} selectivity should decrease. The latter is because the order of oxygen for the carbon oxide formation is higher that that for the C_{2+} hydrocarbon formation (Harold *et al.*, 1992). This is in good agreement with the experimental results

Dependency of the methane conversion on the Al content could be related with the specific surface area; i.e. the increase in the Al content increased the specific surface area and the methane conversion. However, at 1173 K, the increase of reacted methane from the higher extent of Al was not converted to the hydrocarbon compounds, but to carbon monoxide, indicated from the decrease in the C_{2+} selectivity and the increase in carbon monoxide. It was revealed that basic sites are essential for catalyzing OCM by abstracting H from CH_4 molecule (Choudhary *et al.*, 1997) and that the strongly adsorbed oxygen species are essential for the OCM (Tagawa *et al.*, 1998). These properties are characteristics of a p-type conductor. A previous work indicted that a selective anode catalyst should offer the high p-type conductivity ability (Gellings and Bouwmeester, 2000). From the results of the electrical conductivity measurement, addition of Al made the catalyst become less p-type conductive or less basic characteristic. Thus, the selectivity of C_{2+} hydrocarbons decreased.

Considering the C_{2+} yield, it was found that addition of small amount of Al content ($Sm_{1.8}Al_{0.2}O_3$ and $Sm_{1.7}Al_{0.3}O_3$) was able to improve the C_{2+} formation a little. It might be because in the carbon dioxide environment, the high basicity of the catalyst surface like Sm_2O_3 was poisoned readily to form a stable carbonate compound, and the Al content helped prevent the CO_2 poisoning. This effect was reported earlier for other system where addition of Cl and F reduced catalyst basicity and the carbonate formation (Lunsford *et al.*, 1994; Wan *et al.*, 1999). From the CO_2-TPD experiment of the La_2O_3 containing catalyst, it was found that if the carbon dioxide composition was lower than 8.3 kPa at normal pressure (about 8% by volume), the influence of the CO_2 on the catalytic performance was small (Yide *et al.*, 1997). From the experimental results, it was found that $Sm_{1.7}Al_{0.3}O_3$ showed the best C_{2+} yield around 9.5% at conversion and selectivity about 40% and 25%, respectively while $Sm_{1.8}Al_{0.2}O_3$ showed the C_{2+} yield around 9% at conversion and selectivity about 30% and 30%, respectively.

## 5.4 Effect of Operating Parameters

The $Sm_{1.8}Al_{0.2}O_3$ catalyst was selected to investigate the effect of operating parameters (temperature, methane feed composition and feed flow rate) on its catalytic performances (the methane conversion, the C_{2+} selectivity and the C_{2+} yield) and electrical performane (voltage and current) of the SOFC reactor.

5.4.1 Effect of Temperature

The effect of operating temperature on the catalytic and electrical performances of the $Sm_{1.8}Al_{0.2}O_3$ catalyst in SOFC was studied at $T = 1073$, 1123, 1173, 1223 and 1273 K under close circuit condition (without external load). The results are shown in Figures 5.6 (a)-(c). The methane composition of 90.84%, atmospheric pressure and the feed flow rate of 15 ml/min were used in this study.
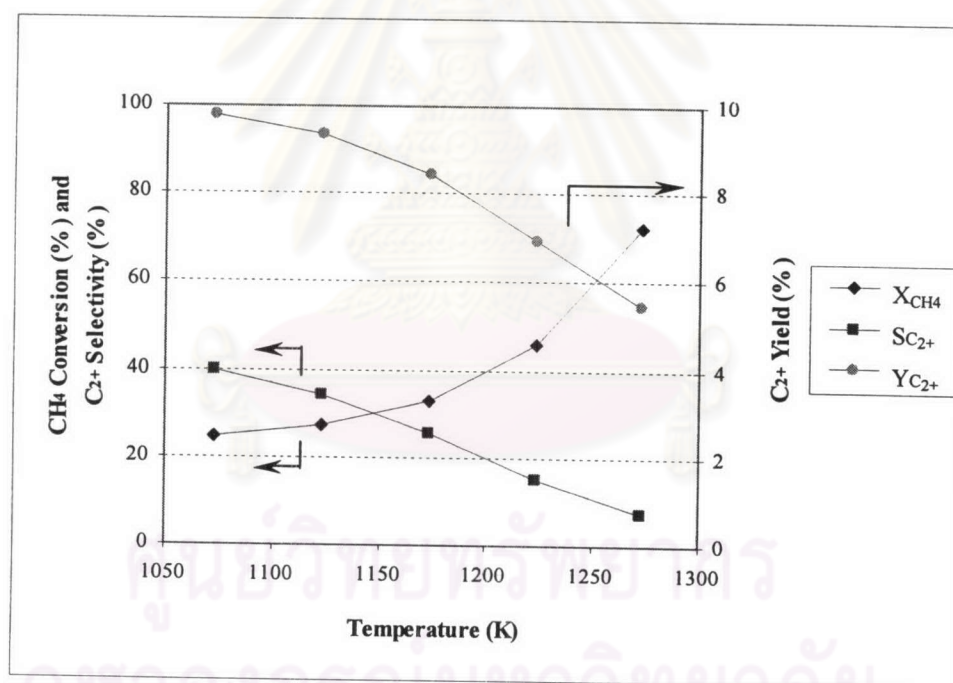
(a)
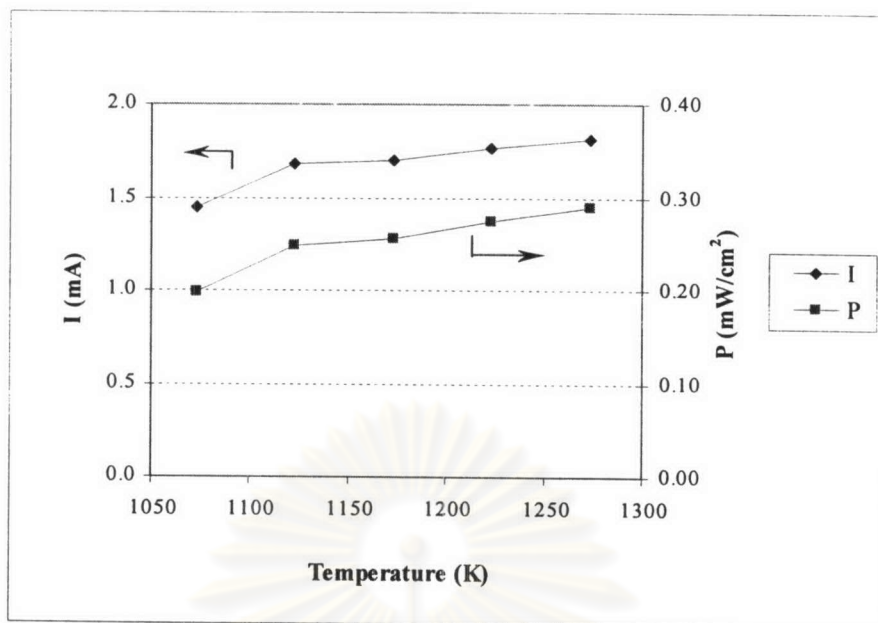
(b)
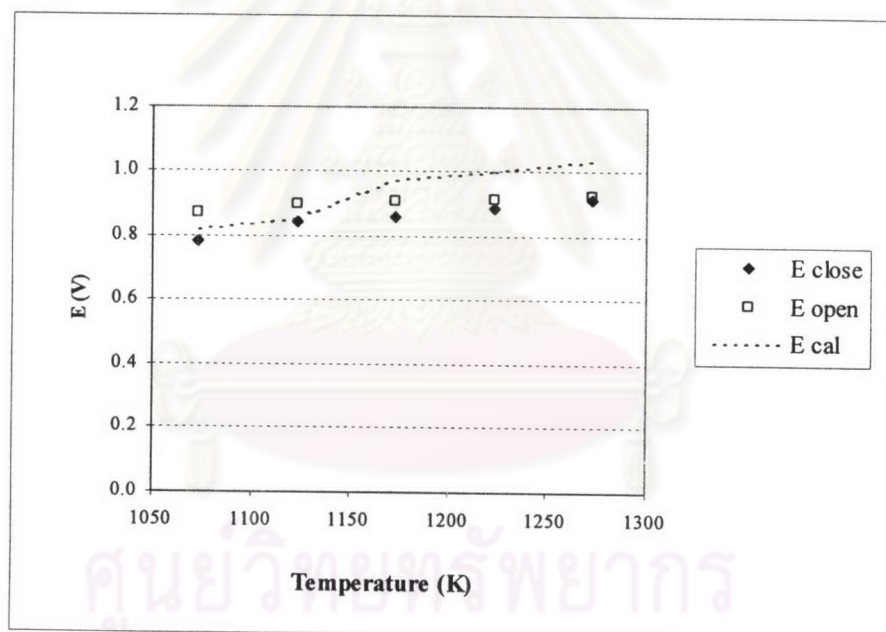
(c)

Figure 5.6 Effect of Temperature on SOFC Performance (a) CH_4 Conversion (X_{CH4}), C_{2+} Selectivity (S_{C2+}) and C_{2+} Yield (Y_{C2+}) at close circuit condition without an external load, (b) Current (I) and Power Density (P) at close circuit condition, and (c) Cell Voltage (E). At Atmospheric pressure, Methane Composition of 90.84% and Methane Flow Rate 15 ml./min.

From Figure 5.6 (a), at close circuit condition (without any external loads), it was found that the conversion and selectivity were very sensitive to temperature, the conversion increased largely according to temperature, from about 20% to 70% when raising the temperature from 1073 to 1273 K, while the C_{2+} selectivity decreased from around 10% to 4.5%. However, at higher temperature, the reaction was tended to incomplete combustion rather than the C_{2+} hydrocarbon formation, resulting in the decrease in the C_{2+} yield. Furthermore, when increasing temperature, the carbon decomposition compound was much increased as indicated by the carbon balance in Table 5.4.

The current also gradually increased when the temperature was increased as shown in Figure 5.6 (b). Theoretically, the higher temperature should make the lower polarization because the resistance to conduction of oxygen ion through YSZ and the resistance to conduction of electrons form the anode catalyst to current collectors were lower at higher temperature. Accordingly, the power outlet increased as the temperature was increased. It was also noticed that the differences in the voltage between the open and close circuit condition were small (Figure 5.6 (c)) even at low temperature. On the other words, the ohmic polarization was small, probably because the electrolyte (YSZ), which is normally the least conductive of the cell component, is slim.

On the other hand, the voltage gradually increased when the temperature was increased at open circuit mode as shown in Figure 5.6 (c). The theoretical voltages (dashed lines) can be calculated by averaging the theoretical voltage of each reaction calculated by Eq. (2.4). It was found that the calculated voltage was close to that from experiment. Therefore, it was able to explain that the increase in temperature caused the increase in voltage due to the change of reaction products according to temperature. It should be noted that CO has higher theoretical voltage than the C_{2+} hydrocarbon.

Table 5.4 Results of Effect of Temperature: Close Circuit Mode

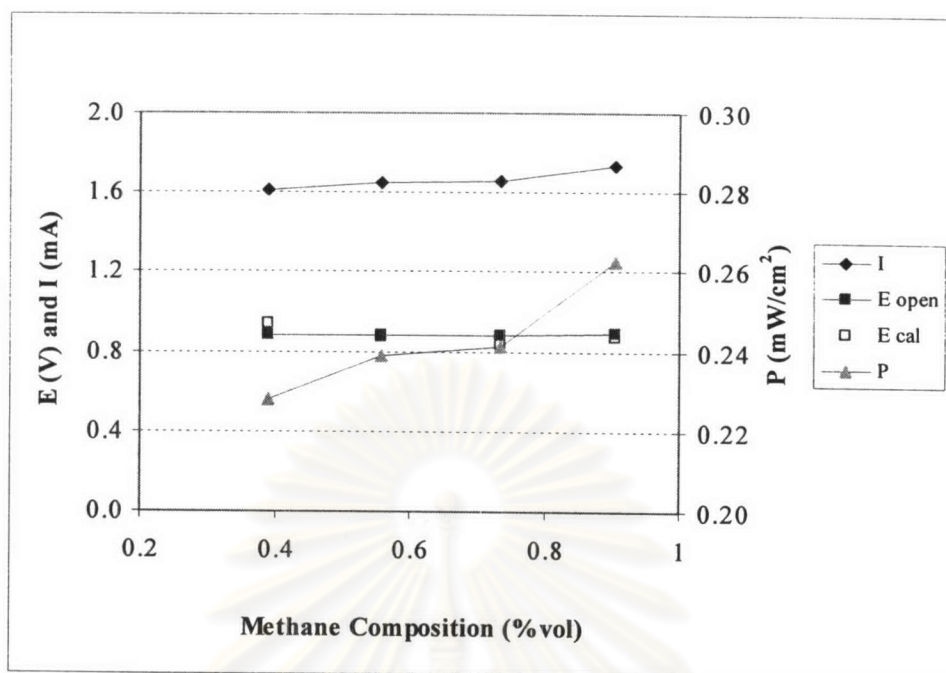| Temp	E	I	CH$_4$ Conversion	Selectivity				C$_{2+}$ Yield
				C$_2$+	CO$_2$	CO	C balance	
K	V	mA	%	%	%	%	%	%
1073	0.781	1.45	24.7	39.6	2.8	0.0	57.6	9.8
1123	0.845	1.68	27.2	34.3	2.6	0.0	63.1	9.3
1173	0.858	1.71	33.1	25.5	3.6	2.1	68.7	8.4
1223	0.889	1.77	45.9	15.1	3.2	14.0	67.7	6.9
1273	0.915	1.82	72.3	7.6	2.5	12.0	77.9	5.5

5.4.2 Effect of Methane Composition

Figures 5.7 (a)-(b) show the results of the effect of the methane composition on the catalytic and electrical performances of the $Sm_{1.8}Al_{0.2}O_3$ catalyst. The experiment was conducted under close circuit condition (without external load), at $T = 1173$ K, atmospheric pressure and the feed flow rate of 25 ml/min.

(a)
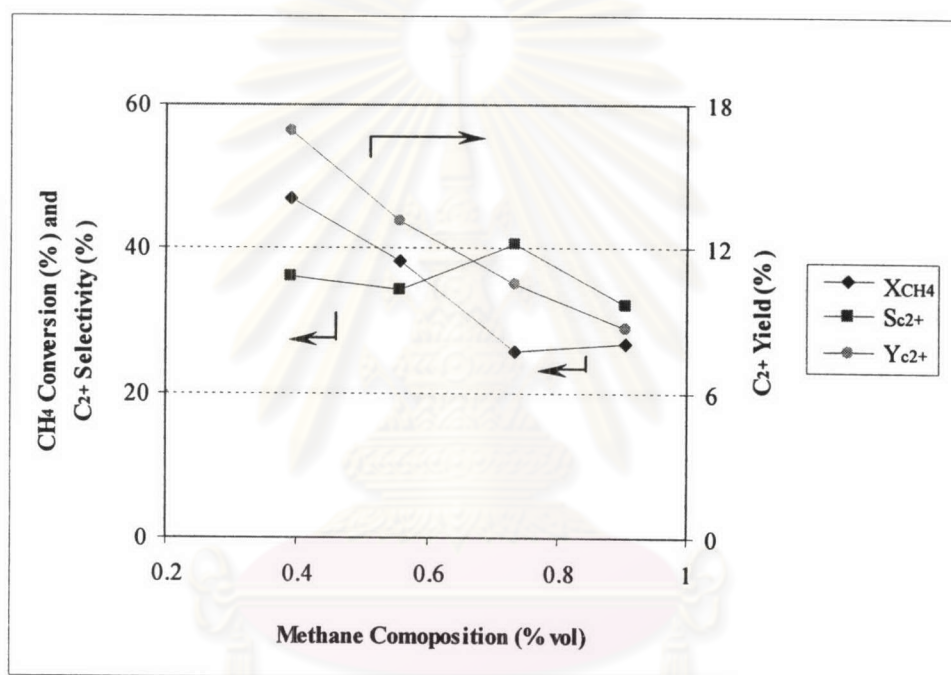
(b)

Figure 5.7 Effect of Methane Composition on (a) CH$_4$ Conversion (X_{CH4}), C$_{2+}$ Selectivity (S_{C2+}) and C$_{2+}$ Yield (Y_{C2+}) at close circuit condition without an external load, and (b) Cell Voltage (E), Current (I) and Power Density (P) (T=1173 K, Atmospheric pressure and Methane Flow Rate of 25 ml/min).

In Figure 5.7 (a) and Table 5.5, it was shown that the methane conversion was decreased remarkably as increasing the methane composition, while the C$_{2+}$ selectivity was slightly changed and CO was apparently decreased, thus resulting in the decrease in the C$_{2+}$ yield. From the kinetic model of some investigations (Al-Zahrani, 2001), the order of methane from the reaction to C$_2$ hydrocarbons was about 0.8-1.0 and that from the reaction to CO$_x$ was about 0.5, as the result, the increase in methane composition caused the increase in the selectivity of C$_2$ hydrocarbon compared to that of CO$_x$. It should be noted that the carbon decomposition compound tended to increase when increasing the methane composition.

According to Figure 5.7 (b), at close circuit condition, the voltage was independent of the change of methane composition because the methane composition

did not significantly determine the reaction routes (or the composition of the products). As a results, when the voltage from the reactions of the production of C_{2+} hydrocarbon, carbon dioxide and carbon monoxide was calculated, the values were not so different as shown in Figure 5.7 (b). At close circuit condition, the current tended to increase slightly as the methane composition increased, causing the small increase in the power outlet.

Table 5.5 Results of Effect of Methane Composition: Close Circuit Mode

Methane Composition	E	I	CH₄ Conversion	Selectivity				C₂₊ Yield
				C₂+	CO₂	CO	C balance	
%	V	mA	%	%	%	%	%	%
39	0.811	1.61	46.8	36.1	4.2	12.7	47.0	16.9
56	0.830	1.65	38.3	34.3	1.6	6.8	57.2	13.1
73	0.834	1.66	25.9	40.5	5.1	3.2	51.3	10.5
90	0.870	1.73	26.9	32.2	3.9	1.2	62.8	8.6

5.4.3 Effect of Gas Flow Rate
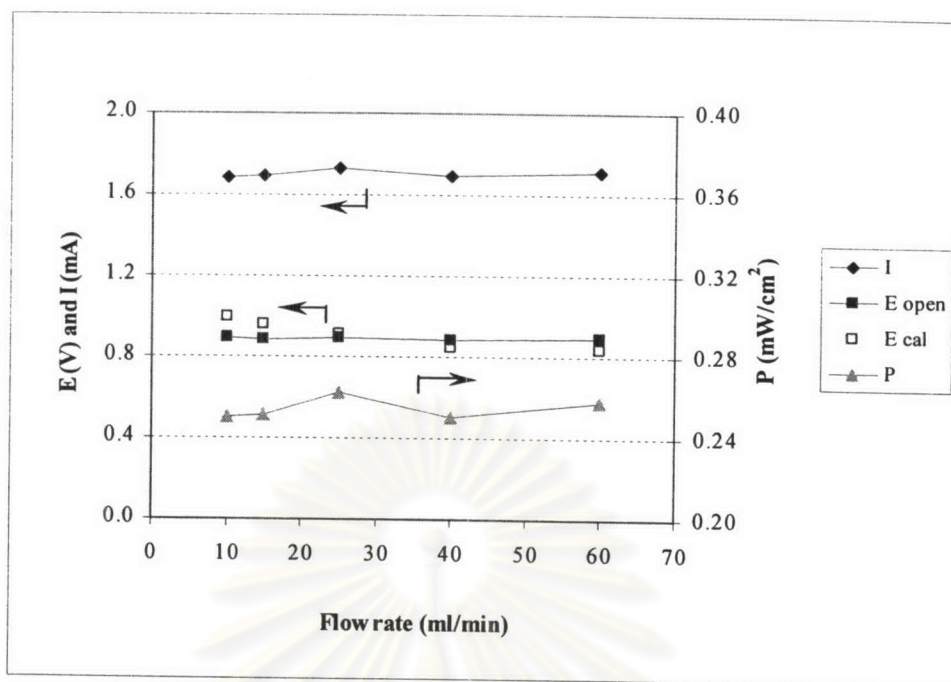
The results of the effect of the gas flow rate on catalytic and electrical performances of $Sm_{1.8}Al_{0.2}O_3$ catalyst are shown in Figures 5.8 (a)-(b). The experiments were conducted under close circuit condition (without external load), at the operation condition of $T = 1173$ K, atmospheric pressure and methane composition of 90.84%.

(a)
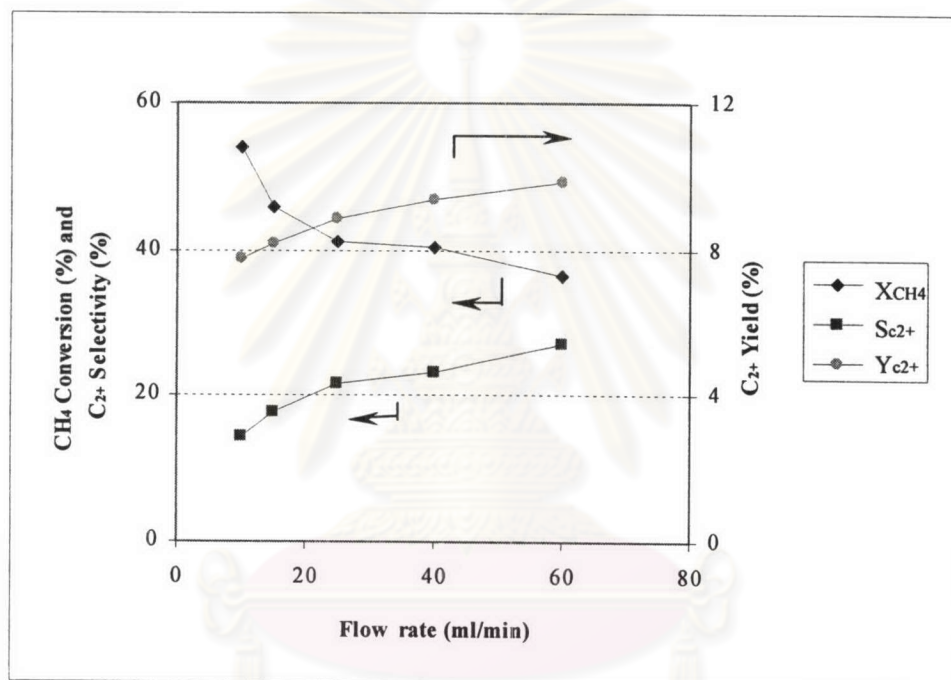
(b)

Figure 5.8 Effect of Gas Flow Rate on (a) CH$_4$ Conversion (X_{CH4}), C$_{2+}$ Selectivity (S_{C2+}) and C$_{2+}$ Yield (Y_{C2+}) at close circuit condition without an external load, and (b) Cell Voltage (E), Current (I) and Power Density (P) (T=1173 K, Atmospheric pressure and Methane Composition of 90.84%).

From Figure 5.8 (a) at close circuit condition (without any external loads), the methane conversion related inversely with gas flow rate, that is, it decreased when gas flow rate was increased (or residence time was decreased), whereas the C$_{2+}$ selectivity increased and the C$_{2+}$ yield also increased gradually with increasing the gas flow rate. It could be noticed that the changes in the conversion and selectivity were sharp at low gas flow rate. From the experiment, the carbon monoxide was not detected at the flow rate more than 25 ml/min and the carbon decomposition compound had no clearly relation with the gas flow rate. It was able to indicate that the higher residence time (lower gas flow rate) resulted in the consecutive reforming reaction of methane with

produced steam according to the reaction (Tagawa *et al.*, 1999) CH_4 (and/or C_{2+}) + H_2O → CO + $3H_2$ and the gas phase combustion of hydrocarbons especially the C_2 hydrocarbons, thus decreasing the C_{2+} formation.

According to Figure 5.8 (b), the voltage and current had no relationship with the gas flow rate, a little change was noticed and the calculated voltages were close to the experiment except at low flow rate (first two points), because at low flow rate, a part of CO was formed by gas phase reaction, which did not use oxygen supplied from electrolyte. The power outlet was thus independent of the gas flow rate. Nonetheless, due to the sharp effect of low flow rate, the effect of flow rate should be noticed at lower gas flow rate range; however, it was not conducted due to limitation of the equipment.