

CHAPTER IV

EXPERIMENTAL

4.1 Electrode Catalyst Preparation

The anode catalyst $\text{Sm}_{2-x}\text{Al}_x\text{O}_3$, abbreviated as SmAlO hereafter, was prepared by following the method described in the previous study (Tagawa *et al.*, 1998). The reagents, $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, were purchased from Aldrich Chemicals and Fluka Chemika respectively. They were weighted and dissolved in distilled water to form a solution (see Appendix A for details of the calculations for preparation of the anode and cathode catalyst). The obtained solution was combusted in a fired stainless steel bowl by dropping a solution at a rate of 40-60 drops per minute. The solid appeared in the bowl was further fired for 1 hour. After being cooling in air, it was ground and sieved on a No.80 mesh.

The cathode catalyst $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$, abbreviated as LSM hereafter, was prepared by the same procedure as mentioned in the anode catalyst preparation. The reagents $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$ and $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were purchased from Fluka Chemika.

4.2 Activity Measurement of SmAlO Catalysts

4.2.1 Methane Pulse Reaction

Activities of a series of $\text{Sm}_{2-x}\text{Al}_x\text{O}_3$ ($x = 0, 0.2, 0.3, 0.5, 0.8$ and 1.0) were tested by using the methane pulse reaction method in a packed bed reactor. The catalyst of 0.2 g was packed into a quartz reactor with 5 mm diameter and then pretreated with air (10 ml/min) at 983 K and atmospheric pressure. After the pretreatment for 16 hr, the catalyst was passed through with the helium gas as a carrier gas at volumetric flow rate of 5.5 ml/min and kept for 15 min. A methane pulse was introduced to the reactor by

using the 90% methane pulse volume of 1 cm^3 at 983 K. Exit gas was analyzed by a gas chromatography.

4.2.2 Fuel Cell Operation

4.2.2.1 Apparatus

Figure 4.1 shows details of the cell assembly of the solid oxide fuel cell reactor. A plate-type YSZ (3 mol% yttria-stabilized zirconia) with thickness of 0.15 mm was used as an electrolyte. A cell of LSM/YSZ/SmAlO was prepared by using a paste method. The anode catalyst of 0.15 g was mixed with glycerol in the ratio of about 1 and then pasted on one side of the electrolyte in a circular shape with the diameter of 2.7 cm. LSM powder of 0.15 g was mixed with glycerol in the ratio of about 1 and then pasted on the other side of the electrolyte opposite to the anode electrode.

The pasted YSZ plate (anode facing down) was placed between two quartz tubes (outer diameter = 36 mm). A pyrex ring was inserted between the YSZ plate and the lower quartz tube to make a seal when heated at high temperature. The other end of the quartz tube was plugged with a rubber bunk to avoid leakage. Feed gas (methane or air) was introduced to the anode surface by using a small quartz tube (outer diameter = 5 mm) inserted through the rubber bunk. The clearance between the end of the small quartz tube and the anode surface was set at 1.5 mm. After the reaction, the product gas was removed from the anode chamber via the other quartz tube inserted in the rubber bunk. The same procedure was used for setting up the cathode chamber except that no pyrex ring was inserted between the end of the quartz tube and the electrolyte. Platinum meshes were contacted to both electrodes to function as current collectors. They were connected to an external circuit through platinum wires. Current and voltage were measured by using an ampere meter and a voltage meter connected in series and parallel, respectively, with the circuit. An external load with various values of resistance was connected in series with the circuit in order to adjust the current density while operating the cell.

To compare the activities of the SmAlO₃ catalysts with various compositions, the cell was operated under different values of external load and temperature ($T = 1173$ and 1273 K). The schematic diagram of the experimental setup for the solid oxide fuel

cell reactor is shown Figure 4.2. The SOFC reactor was heated up to a desired temperature by an electric furnace with a temperature-programmed controller. Gas flow rates were controlled by needles valves.

4.2.2.2 Operation Procedure

Catalyst Pretreatment

- The reactor was heated up with a heating rate of 2 K/min from room temperature to 1173 K, under air flow and atmosphere pressure.

- The anode and cathode catalysts were then pretreated in air (air flow rate = 10 ml/min) at 1173 K for 3 hr.

- After the pretreatment, helium gas was introduced to replace air in the anode side.

Leakage Test

- After the anode chamber was purged with helium for approximately 1 hr, the reactor was checked for leakage by comparing the oxygen content between the inlet and outlet of the reactor.

Operation

- The 90.84% methane gas started feeding to the anode side at the flow rate of 15 ml/min.

- The reactor was set at open circuit condition and held for 1 hr.

- Gas products from the anode chamber were sampled for analysis of its composition by a gas chromatography, and the voltage was recorded from the voltage meter.

- The reactor was changed to close circuit condition, where the current was adjusted by the external load.

- The exit gas was analyzed by the gas chromatography, and the voltage and current were recorded from the voltage and ampere meter respectively when reaching steady state condition which took approximately 1 hr.

- The catalytic activity of the catalysts and the power energy outlet for all anode catalysts were measured at temperature 1173 and 1273 K.

- The catalytic activity of the catalyst was shown in terms of

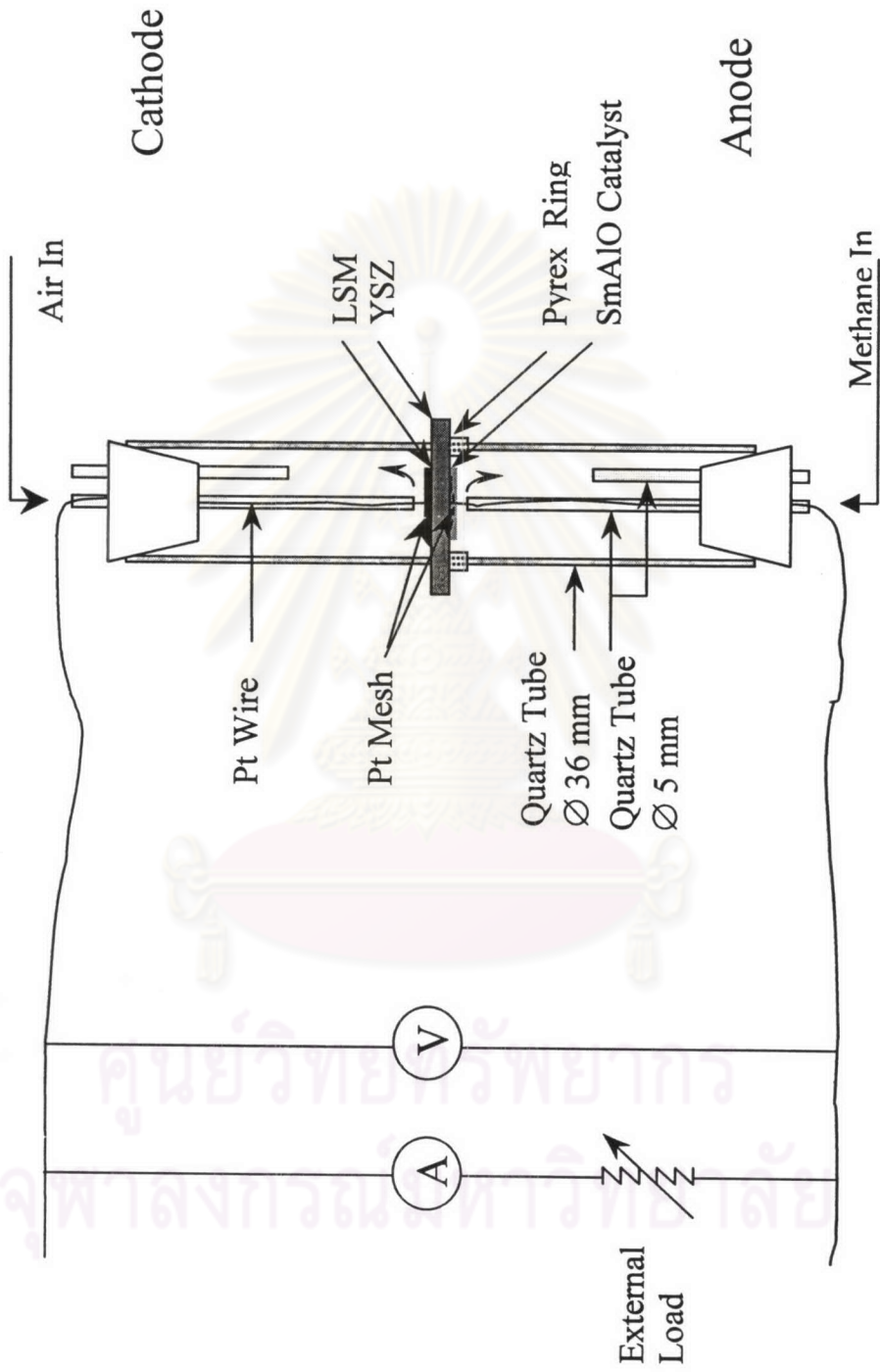


Figure 4.1 Solid Oxide Fuel Cell Reactor

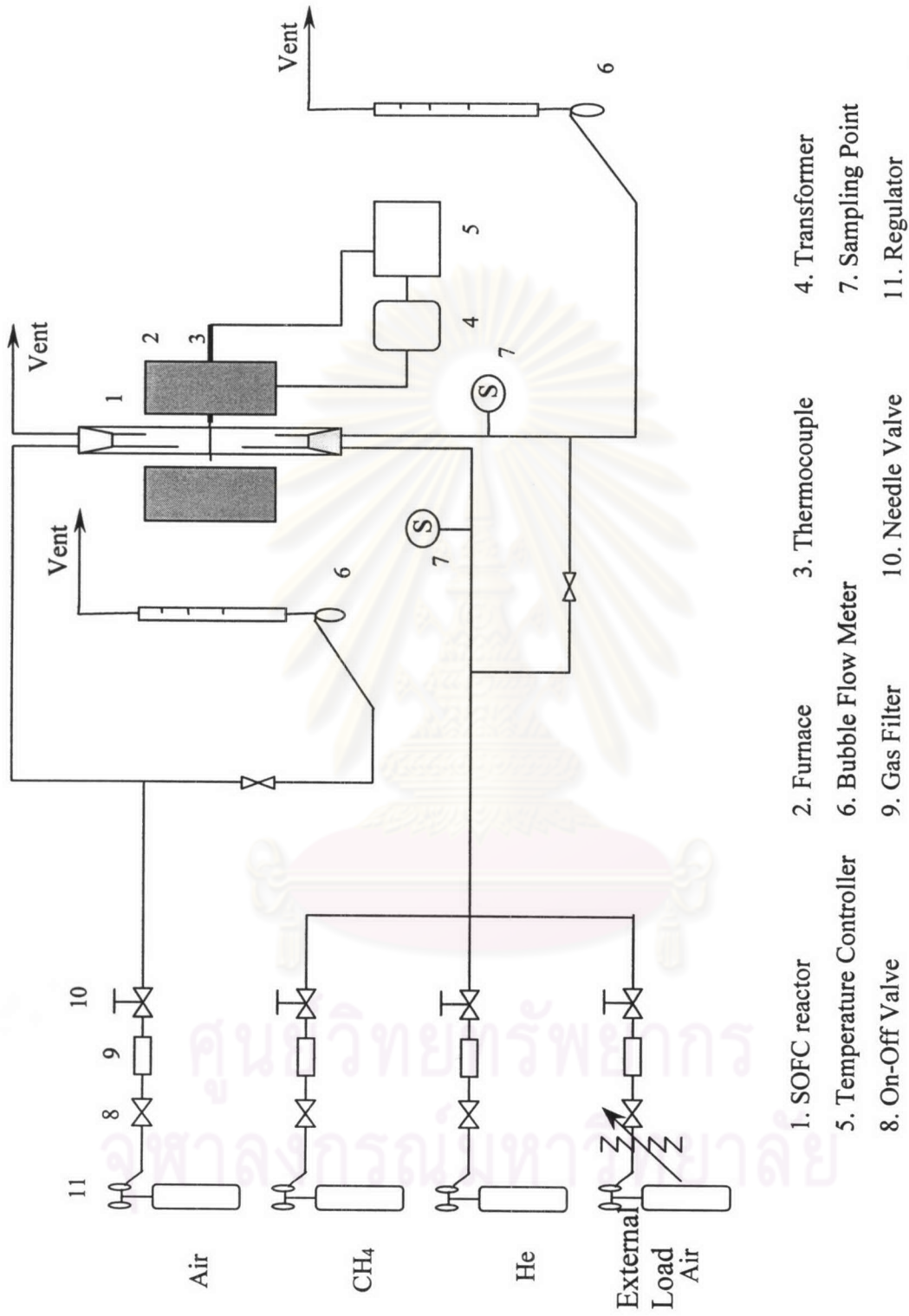


Figure 4.2 Schematic Diagram of Experiment Set-up

$$\% \text{Conversion} = \frac{\text{flow rate of reactant in} - \text{flow rate of reactant out}}{\text{flow rate of reactant in}} \times 100$$

$$\% \text{Selectivity} = \frac{\text{flow rate of product out}}{\text{flow rate of reactant in} - \text{flow rate of reactant out}} \times \frac{\text{mole of reactant}}{\text{mole of product}} (\text{in stoichiometry}) \times 100$$

$$\% \text{Yield} = \frac{\% \text{Conversion} \times \% \text{Selectivity}}{100}$$

4.2.3 Analytical Instrument

Products of the OCM reaction from the methane pulse pretest and the SOFC reactor were analyzed by Shimadzu gas chromatographs. Hydrocarbon gases were detected by GC-14B with FID detector while carbon dioxide and carbon monoxide were detected by GC-8A with TCD detector. In addition, oxygen content during cell leakage test was analyzed by GC-8A with TCD detector. The conditions of gas chromatographs were summarized in Table 4.1.

Table 4.1 Operating conditions of gas chromatographs

Gas Chromatograph	Shimadzu GC8A	Shimadzu GC14B
Detector	TCD	FID
Column	MS-5A, Porapak-Q	VZ10
Carrier gas	He (99.9999%)	N ₂ (99.9999%)
Carrier gas flow rate	25 ml/min	25 ml/min
Column temperature		
- Initial	100 C	60 C
- Final	100 C	60 C
Detector temperature	130 C	110 C
Injector temperature	130 C	110 C
Analyzed gas	CO, CO ₂	Hydrocarbon C ₁ -C ₄

4.3 Catalyst Characterization

4.3.1 Specific Surface Area by BET

The apparatus consisted of two gas feed lines for helium and nitrogen. The flow rate of gas was adjusted by means of a fine-metering valve. The sample cell was made of pyrex glass. The operation conditions of the gas chromatograph (GOW-MAC) are shown in Table 4.2.

Mixture of helium and nitrogen gas flowed through the system at the nitrogen gauge pressure of 0.3. The sample, which was pretreated at 1173 K in air for three hours, was placed in the sample cell. The sample was then dipped into the liquid nitrogen. Nitrogen was adsorbed on the surface of the sample until equilibrium was reached. After that, the nitrogen-adsorbed sample was dipped into the water at room temperature. The adsorbed nitrogen was desorbed from the surface of the sample. This step was completed when the recorder line returned back to the base line. The specific surface area was calculated according to Appendix B.

Table 4.2 Operation Condition of Gas Chromatograph (GOW-MAC)

Model	GOW-MAC
Detector	TCD
Helium flow rate	30 ml/min
Detector temperature	35 C
Detector current	80 mA

4.3.2 Crystallization of Catalyst by XRD

Structures of the SmAlO anode catalysts were identified by X-ray diffraction technique, by Siemens D 5000 X-ray diffractometer, using $\text{CuK}\alpha$ radiation with Ni filter in the 2θ ranges of 20-80°.

4.3.3 Electrical Conductivity of Anode Catalyst

Anode catalyst of 0.8 g was pressed under the pressure of 300 kg/cm² for 10 min and then cut into the dimension of 6×12×1 mm. The pressed catalyst was connected with platinum wires and then brought into the quartz tube. The platinum wires were then connected to a DC power supply, and the voltage and ampere meter were connected in series and parallel to the DC power supply, respectively. Before measurement of the electrical conductivity, the catalyst was pretreated under the flowing air at the temperature 1173 K for 3 hr.

The electrical conductivity of the catalyst was measured by applying the direct current to the piece of the catalyst and measuring the currents at various voltage levels. The electrical conductivity was calculated from the inverse of the slope of the voltage/current plot. The electrical conductivity was tested under nitrogen gas with oxygen content of 1 % at temperature from 1023 to 1273 K.



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