

CHAPTER IV

EXPERIMENTAL

This chapter describes the experimental procedures. Details are given for the experimental set up of the solid oxide fuel cell type reactor, electrode preparation method, fuel cell type temperature-programmed desorption (FC-TPD) measurement, oxygen permeation study and OCM reaction for C2 and electricity production study.

4.1 Apparatus

The schematic diagram of the solid oxide fuel cell type reactor was illustrated in Figure 4.1. A tube-type YSZ membrane (8 mol% Y_2O_3 , thickness = 1.5 mm, inside diameter = 18 mm, outside diameter = 21 mm, length = 500 mm, effective surface area = 0.0148 m^2) was used as an electrolyte. $La_{1.8}Al_{0.2}O_3$ (abbreviated as LaAlO) prepared by a mist decomposition method was used as an anode catalyst on the inner surface of the tube while $La_{0.85}Sr_{0.15}MnO_3$ (abbreviated as LSM) prepared by a conventional paste method on the outer side was used as the cathode. Platinum wire was connected to platinum meshes placed on both electrode surfaces to serve as current collectors. Current meter and voltmeter were used to measure closed circuit current (CCI) and open circuit voltage (OCV), respectively. Voltages at various current values were measured using a potentiostat.

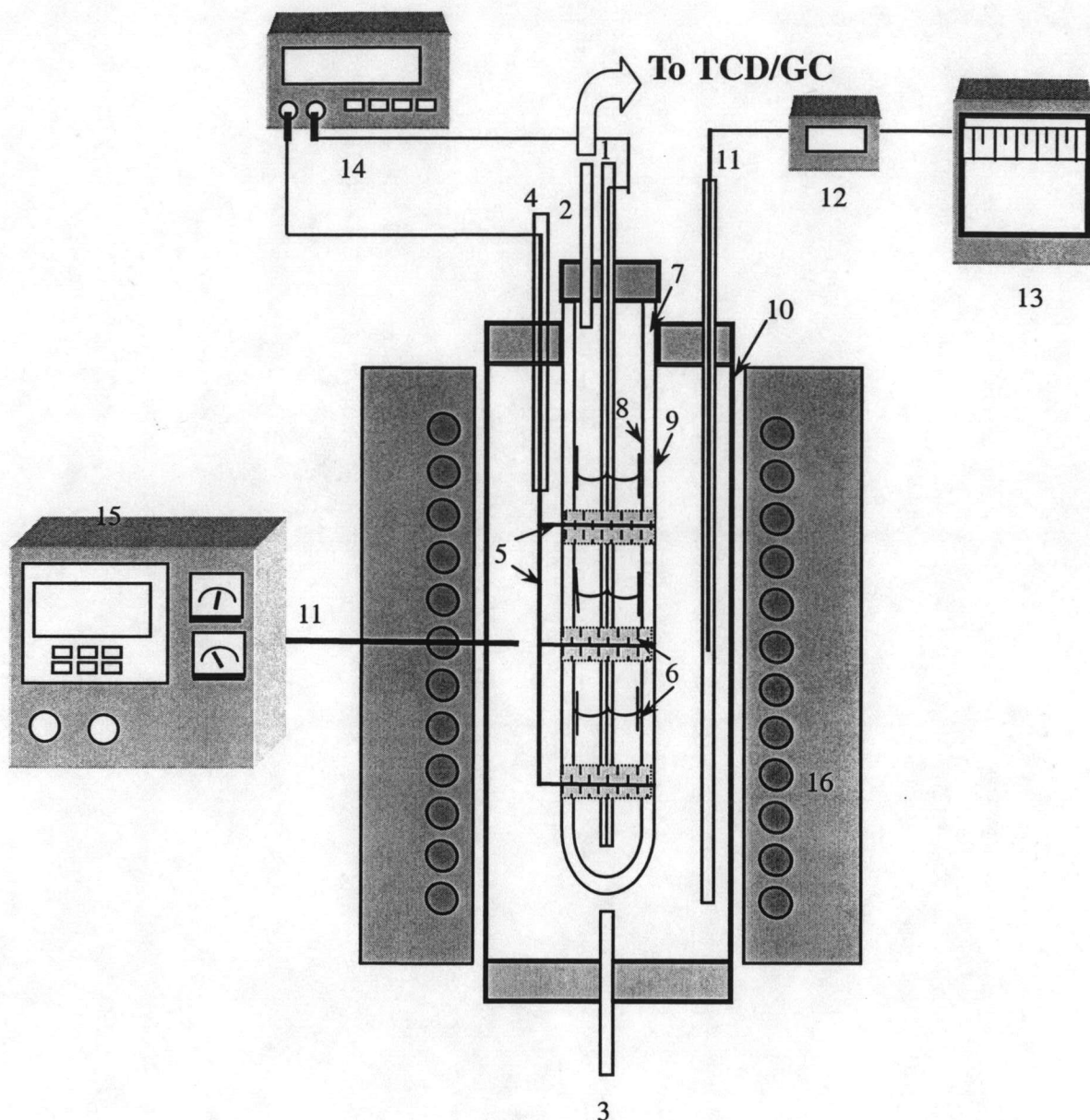


Figure 4.1 Schematic diagram of the solid oxide fuel cell type reactor

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|-------------------------------|------------------------------------|--------------------------------|
| 1. Anode side feed (Air/He) | 2. Exit gas from anode side | 3. Cathode side feed (O_2) |
| 4. Exit gas from cathode side | 5. Platinum wire | 6. Platinum mesh |
| 7. YSZ tube | 8. Anode ($LaAlO_3$) | 9. Cathode (LSM) |
| 10. Quartz tube | 11. Thermocouple | 12. Temperature indicator |
| 13. Temperature recorder | 14. Ammeter/Voltmeter/Potentiostat | |
| 15. Temperature controller | 16. Furnace | |

4.2 Electrode preparation method

4.2.1 Anode preparation

LaAlO anode material was prepared on the inside of YSZ tube by the mist pyrolysis method as follows (Tagawa *et al.*, 1999, 2003). Figure 4.2 shows the setup for the anode preparation. A mixed aqueous solution of lanthanum nitrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) and aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), (La:Al=9:1) was placed in a reservoir. With a ceramic ultrasonic transducer (1.7MHz), mist of solution was generated. The mist was delivered to YSZ tube with the air flow using an aspirator. YSZ tube was placed in a furnace and heated. The pyrolysis was generally operated in periodic operations. In this periodic operation, the mist was intermittently sprayed to YSZ tube and the optimum condition was summarized in Table 4.1.

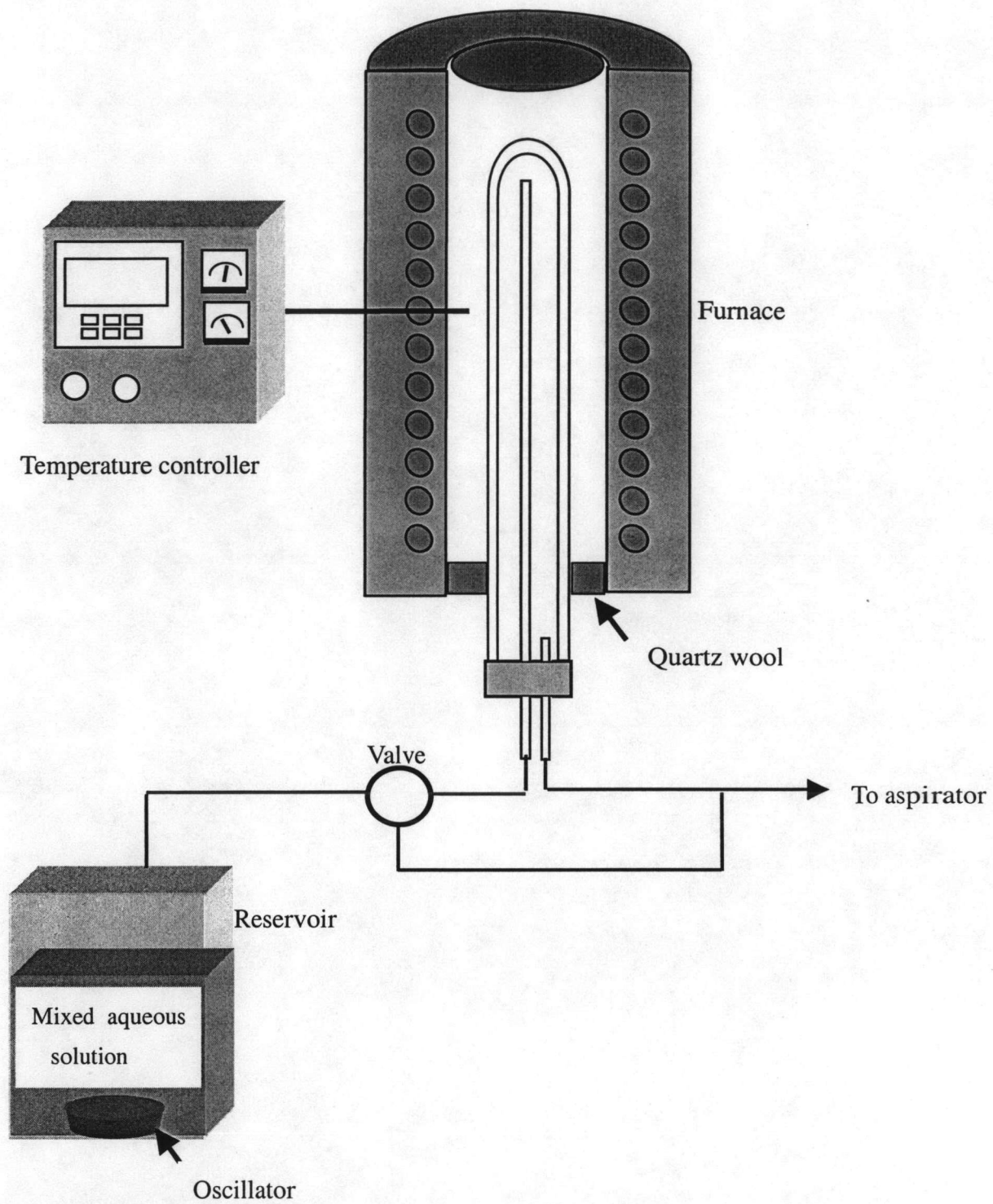


Figure 4.2 Schematic diagram of the setup for the anode preparation

Table 4.1 Optimum condition for the anode preparation

YSZ temperature	503 K
Concentration of salt solution	1.25 wt%
Spray time	30 s
Interval time	30 s
Total spray time	2 h

4.2.2 Cathode preparation

Mixed aqueous solution of lanthanum nitrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) 15.72 g, strontium nitrate ($\text{Sr}(\text{NO}_3)_2$) 1.355 g and manganese nitrate ($\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) 12.26 g were diluted in 100 ml of distilled water and then slowly charged as droplets into a red-heated quartz crucible. $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ (abbreviated as LSM) with perovskite structure was obtained and pounded to fine powders. LSM powder was mixed with glycerol and pasted into thin film on the outside of YSZ tube and heated at 1223 K for about 3 h in air (Tagawa *et al.*, 1999, 2003).

4.3 Fuel cell type temperature-programmed desorption (FC-TPD) measurement

The outlet gas from the anode side was directly connected to a thermal conductivity detector (TCD). A potentiostat was used to supply an external electrical potential to the system. Oxygen transport from the cathode side to the anode was promoted under the applied positive potential.

Before FC-TPD measurement, the cell was pretreated under the following condition: the air flow rate in the anode = $1.36 \times 10^{-5} \text{ mol.s}^{-1}$, the oxygen flow rate in the cathode = $1.02 \times 10^{-5} \text{ mol.s}^{-1}$ and $T = 1273 \text{ K}$. Three modes of pretreatment; i.e., open

circuit pretreatment, closed circuit pretreatment and closed circuit pretreatment with applied potential (V_P), were considered in this study. After the pretreatment for 7 h, the sample was slowly cooled down to $T = 600$ K at a rate of 0.093 K.s^{-1} under the pretreatment gases. Then, the anode gas was switched to helium carrier gas ($1.36 \times 10^{-5} \text{ mol.s}^{-1}$) while the cathode gas remained unchanged. The applied potential (V_P) was disconnected for the closed circuit pretreatment. The anode exit gas was analyzed using TCD. After the baseline was stabilized, FC-TPD measurement was started by increasing the temperature at a desired rate ($\beta = 0.05, 0.083, 0.117$ and 0.133 K.s^{-1}). The rate of temperature increase (β) was determined within the range of good reproducibility of TPD spectra. With these β values, no apparent peak widening which disturbed the analysis was observed. Oxygen spectra were recorded by TCD. There were three modes of FC-TPD measurement; i.e., open circuit FC-TPD, closed circuit FC-TPD and closed circuit FC-TPD with applied potential. In the closed circuit mode, both electrodes were connected to allow oxygen permeation from the cathode to the anode. An external potential (V_T) can be supplied to the cell by the potentiostat during the closed circuit mode.

4.4 Steady state oxygen permeation study

Steady state oxygen permeation measurements were performed at various temperature levels: i.e., $T = 1073, 1123, 1173, 1223$ and 1273 K. Helium ($1.36 \times 10^{-5} \text{ mol s}^{-1}$) and oxygen ($1.02 \times 10^{-5} \text{ mol s}^{-1}$) were fed to the anode and the cathode, respectively. The outlet gas from the anode side was directly connected to a gas chromatograph for analysis of gas composition. The oxygen permeation flux was calculated from the flow rate and composition of the anode exit gas. The flow rate and its composition was measured and analyzed by a bubble flow meter and a gas chromatograph with TCD

detector, respectively. Sampling was conducted every 5 min until reaching to a steady state condition (approximately 0.5 h). Another set of steady-state oxygen permeation was carried out by using methane ($6.8 \times 10^{-6} \text{ mol s}^{-1}$) as an anode reactant gas at various temperature levels: i.e. $T = 1073, 1123, 1173, 1223$ and 1273 K . In this case, permeated oxygen has reacted with methane to produce oxygen containing species such as CO, CO₂ and H₂O. Thus, the oxygen permeation flux was estimated by analyzing these oxygen containing products. The steady state measurements for both sets of experiments were carried out at various levels of the applied potential.

4.5 OCM for C2 and electricity production study

The standard operation was as follows. Methane ($3.4 \times 10^{-6} \text{ mol s}^{-1}$) was fed to the anode without dilution gases. Oxygen or air ($1.02 \times 10^{-5} \text{ mol s}^{-1}$) was fed to the cathode. The operating temperatures were varied: i.e. $T = 1073, 1123, 1173, 1223$ and 1273 K . The flow rate of the anode exit gas was measured and its composition was analyzed by a gas chromatography with TCD detector every 30 min until reaching a steady state condition.