CHAPTER IV

CONCLUSION AND RECOMMENDATION

6.1 Conclusion

Oxidative coupling of methane (OCM) in LSM/YSZ/LaAlO solid oxide fuel cell (SOFC) type reactor for C2 hydrocarbons and electricity co-generation was studied in this research. The following conclusions can be drawn from the investigation.

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

(a) The fuel cell type temperature-programmed desorption (FC-TPD) measurements of oxygen enables to discuss the oxygen species for the combustion reaction and the coupling reaction separately. They are corresponding well with those obtained from TPD of powder LaAlO sample in previous work (Tagawa *et al.*, 2003).

(b) An increase of the applied potential during the pretreatment increases the amount of desorbed oxygen especially at temperature lower than 1250 K. This suggests that the applied potential can activate the anode material (LaAlO) on oxygen adsorption.

(c) The activation energy of desorption decreases with increasing the applied potential during the pretreatment for both sites, suggesting the qualitative change of adsorption site with the electrostatic field.

6.1.2 Oxygen permeation through the LSM/YSZ/LaAlO cell

(a) The oxygen permeation flux through LSM/YSZ/LaAlO cell of SOFC reactor is 8.90×10^{-8} mol m^{-2} s^{-1} at 1173 K with an activation energy of 170 kJ mol^{-1}.

(b) Increasing the applied potential increases the oxygen permeation fluxes in one order of magnitude and reduces the activation energy of the oxygen permeation.

(c) The oxygen permeation fluxes under the methane feed are 1-2 orders of magnitude higher than those under the helium feed.

(d) Using the parameters obtained from both literature and fitting parameters, a model of oxygen permeation was proposed.

(e) In the helium case, the oxygen permeation at LaAlO anode is the rate-limiting step for the oxygen permeation.

(f) When changing helium to a reactive gas as methane, the resistances in the three parts (LSM/YSZ/LaAlO) become comparable.

6.1.3 OCM in SOFC reactor for C2 hydrocarbon and electricity co-generation

(a) Methane conversion and C2 selectivity increase with increasing operating temperature. The methane conversion and C2 selectivity were 23.7% and 91.7% at 1273 K with the optimum preparation of anode catalyst.

(b) A set of reaction model was proposed with distinguished two different oxygen species, i.e., oxygenate and coupling species which is useful in evaluating the OCM in SOFC type reactor.

(c) The internal resistance of a cell could be lumped and estimated by the maximum power transfer theorem.

$$R_{\text{int}} = \frac{0.0567}{P_{\text{O}_2,\text{CA}}^{0.2} P_{\text{CH}_4}^{0.51} T} \exp\left(\frac{166000}{R_{\text{g}} T}\right)$$

(d) Increasing the external load decreases the oxygen transport, resulting in decreased methane conversion. However, C2 selectivity was almost constant.

(e) No effort for oxygen purification is required for the system.

(f) The maximum power density obtained with pure methane feed at atmospheric pressure and 1273 K is 3.34 W m^{-2}. This value is in the same range as those reported by other SOFC reactor investigators (Guo *et al.*, 1999; Tagawa *et al.*, 1999). However, this value is quite far from typical SOFC which is mainly used for power generation.

(g) Methane conversion increases with decreasing total molar flow rate or decreasing methane feed concentration while C2 selectivity is only slightly decreased.

(h) An operation at higher pressure seems to be attractive to obtain higher power and C2 production.

6.2 Recommendation and future work

(a) As the results suggest that our SOFC system is a good reactor for C2 production where electric power is generated simultaneously as the byproduct, the comparative study of the performances of others reactors, i.e., fixed-bed reactor (FBR), porous membrane reactor (PMR), mixed ionic and electronic conducting reactor (MIECR) for OCM to C2 hydrocarbons should be investigated. Figure 6.1 shows configurations of the proposed reactor for C2 hydrocarbons production. For FBR, methane, oxygen/air and inert gas are mixed and co-fed to an impermeable tube reactor. The membrane reactors are a double tubular reactor as shown in Figure 6.1 (b)-(c). The inner tube may made be of a γ-alumina membrane (for PMR) or $La_{0.40}Sr_{0.60}Ga_{0.40}Fe_{0.60}O_{3-\delta}$ (for MIECR). The outer shell is made of an impermeable wall.

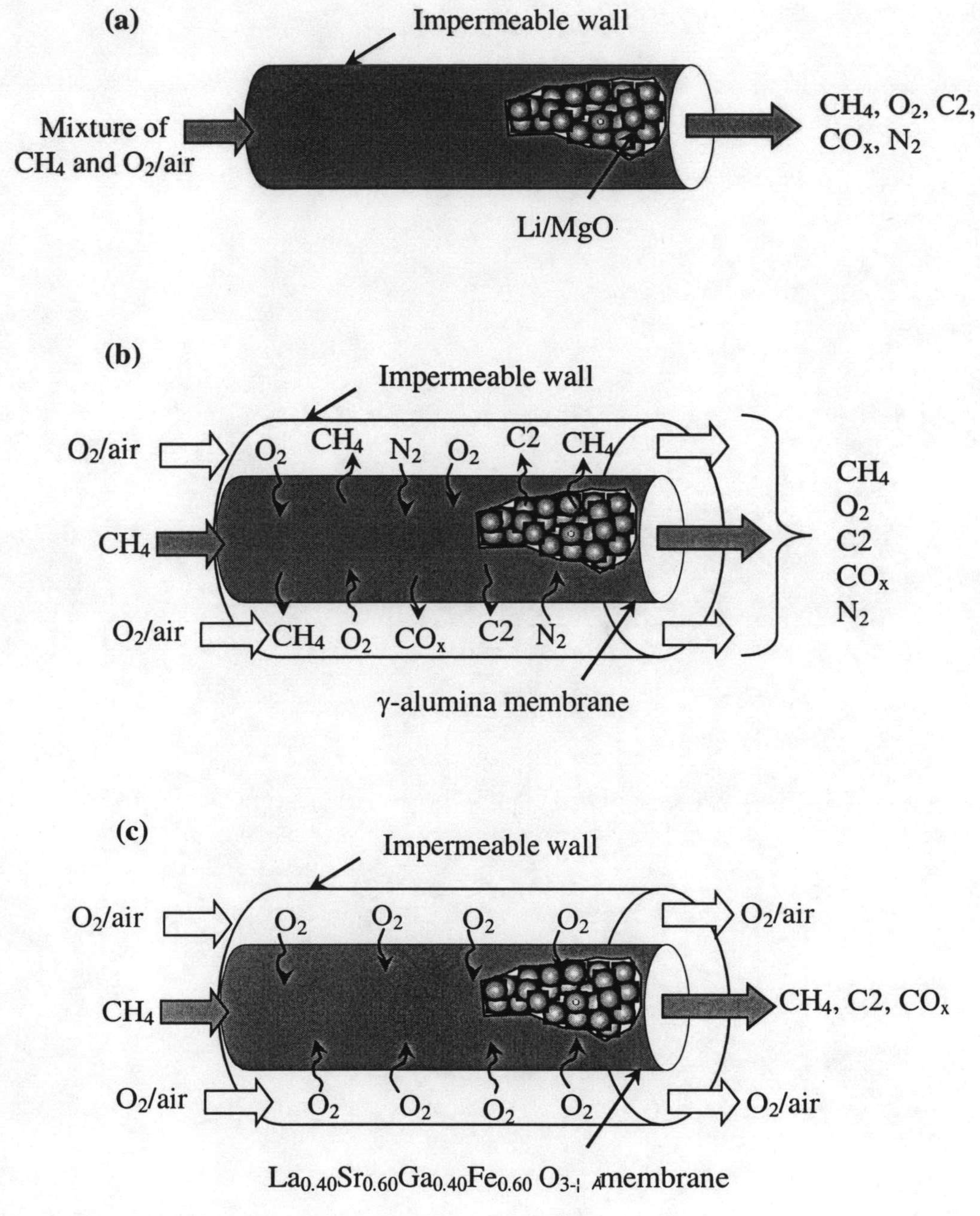

Figure 6.1 Proposed schemes for various OCM reactors (a) FBR (b) PMR and (c) MIECR.

(b) This work is limited to the simulations for C2 and electricity production operated at maximum power transfer. In the electrical engineering view point, if the equivalent circuit can be drawn from the chemical reaction in SOFC reactor, the generation of power and also C2 production rate at different part load operation could be estimated. The cell voltage could be derived from many reactions, and the main reaction of C_2H_6 to C_2H_4 possibly governed it; however, the relationships between them are still unclear. Considering electric current, it is clear that it is the summation of current generated from each reaction. The current generated from each reaction (I_1 –I_5) is directly proportional to the oxygen consumption in their reaction by using Faraday's law. The internal cell resistance obtained from this work may be considered in three part; cathode, electrolyte and anode resistances. Apart from the effect of temperature and oxygen partial pressure on resistance in each part, cathode and electrolyte resistance may depend on their electronic and ionic conductivity, respectively. The rough idea for equivalent circuit could be proposed in Figure 6.2. E_1 to E_5 are calculated from the reactions shown in Eqs. (5.25)-(5.29) using Eq. (2.1). I_1 to I_5 can be calculated from reaction Eqs. (5.25)-(5.29) using Eq. (5.44).

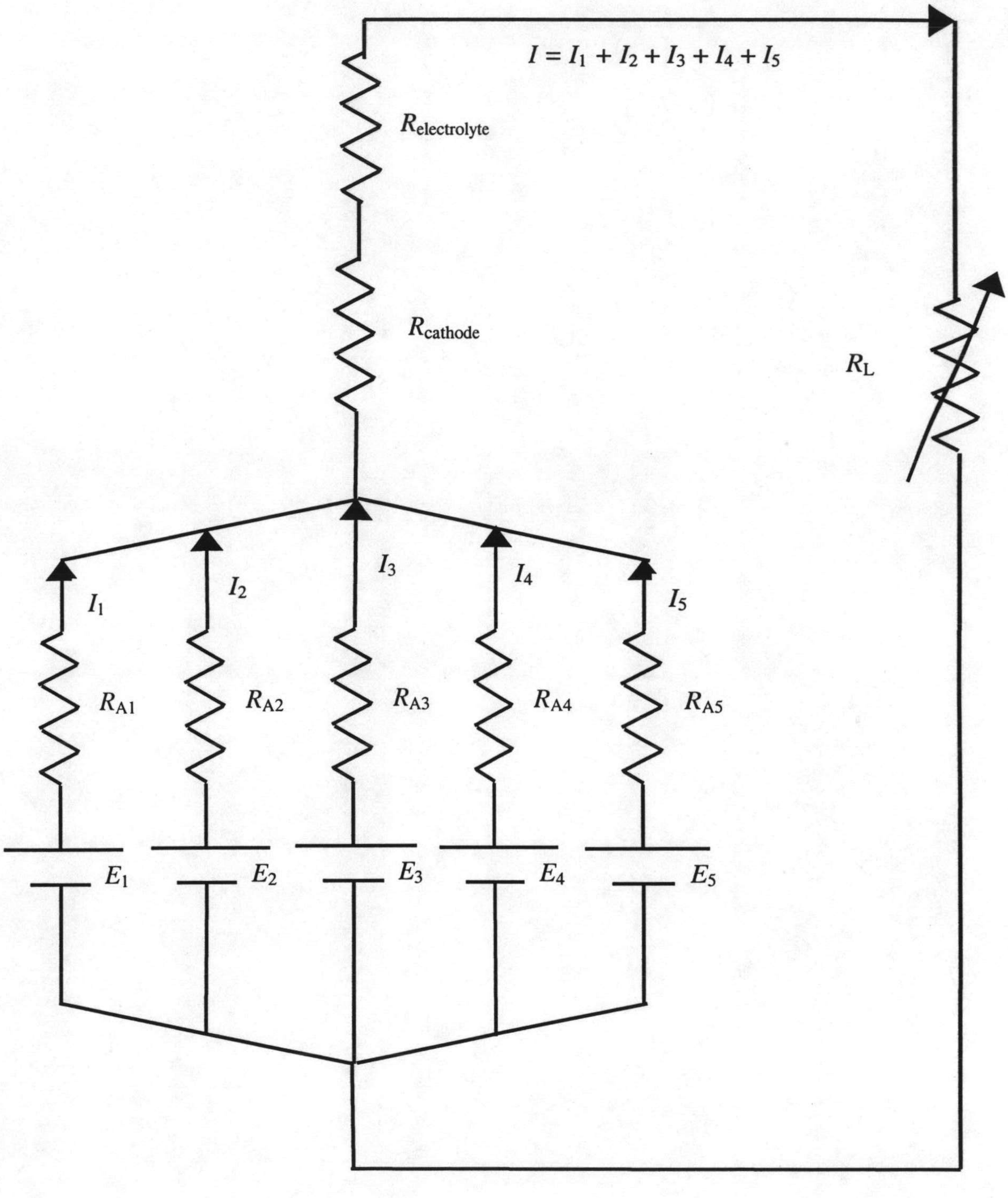

Figure 6.2 Proposed equivalent circuit of SOFC reactor for OCM.

(c) Our SOFC system in this thesis operates at high temperature as 1273 K. Nowadays, many efforts have been focused on reducing the cost of SOFC, by lowering the operating temperature to intermediate temperature about 873-1073 K or reducing the production cost. As shown in the permeation model, the oxygen permeation resistances in the three parts (LSM/YSZ/LaAlO) are comparable. Decreasing of resistance in any part may improve the reactor performance. The electrochemical vapor deposition (EVD) has been developed to produce thin layer of electrolyte and electrode which is now used commercially. However, this method is generally very expensive because they involve the use of sophisticated reactors and/or vacuum systems. A novel method of Flame Assisted Vapor Deposition (FAVD) has been proposed to deposit LSM cathode on YSZ electrolyte (Charojrochkul *et al.*, 2004a, b). This method combines flame synthesis and vapor deposition methods. The liquid precursor undergoes a combustion process into a vapor phase, and then deposits as an oxide film on a substrate.

Regarding YSZ electrolyte preparation, among various developed processes, slurry coating processes (e.g. dip coating, screen printing and spin coating) have been proved to be one of the most cost-effective processes (Cai *et al.*, 2002; Zhu *et al.*, 2005).

The application of these processes may significantly improve the reactor performance.

(d) As mentioned above, the reaction rate is strongly dependent on operating temperature which is mainly related to types of oxygen species. How to control the species of active oxygen for OCM should be of serious concern. The oxygen species may not only depend on types of anode catalyst but also their morphology. Atomic force microscope (AFM) offers the possibility for obtaining atomic-resolution images with a minimum of prior preparation of samples. As a raster-scan drags the tip over the sample, some sort of detection apparatus measures the vertical deflection of the cantilever, which indicates the local sample height on the atomic scale (Vickerman, 1998). In order to investigate the oxygen species, since difference in oxygen ion posses different electron spin. Electron spin resonance (ESR) is the chief application in the study of free radicals at very low concentration (Ewing, 1987).

These techniques may be applied and, consequently, offer the possibility of discussion on the effect of oxygen species on C2 selectivity and the effect of applied potential on oxygen species and their desorption characteristics.