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공학석사학위논문

**A Start-Up Strategy of Molten Carbonate
Fuel Cell and Internal Combustion Engine
Hybrid System for Distributed Power
Generation**

분산발전용 용융탄산염 연료전지와 IC 엔진의
하이브리드 시스템 시동 시나리오 개발

2013 년 8 월

서울대학교 대학원

기계항공공학부

정 지 영

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지도교수 송 성 진

이 논문을 공학석사 학위논문으로 제출함

2013 년 8 월

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Abstract

A Start-Up Strategy of Molten Carbonate Fuel Cell and Internal Combustion Engine Hybrid System for Distributed Power Generation

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A start-up strategy for molten carbonate fuel cell (MCFC) and internal combustion (IC) engine hybrid system, previously developed by the authors, has been developed to validate its operability. Because only design point operation of hybrid system was studied in previous research, adequate start-up strategy for MCFC-IC engine hybrid system is needed. To analyze the start-up strategy, start-up process of this hybrid system has been divided into 4 stages. The first two stages compose the heat-up process to preheat the MCFC from ambient to the operating temperature

(~570 °C). The required heat for fuel cell is provided from the IC engine exhaust heat because the IC engine generates heat as well as power during the heat-up process whereas the MCFC does not generate any power. During the first heat-up stage, nitrogen flows into the fuel cell to prevent corrosion after the long time operating. When the MCFC temperature reaches 500°C, the second heat-up stage begins, and fuel start to flows into the fuel cell to prepare for power-up process. The next two stages following heat-up process compose the power-up process. During the power-up process, power is generated from both the MCFC engine as well as the IC engine. According to the operable range of each component, the power-up process is composed of the MCFC-SI engine stage and the MCFC-HCCI engine stage. Thus, the hybrid system is independently operable from the start-up to the full load operation without a need for either an electric heater or a catalytic burner.

Keywords: MCFC; HCCI engine; SI engine; Hybrid system; Start-up strategy

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Contents

Chapter 1 Introduction	1
1.1 Distributed power generation	1
1.2 Previous researches	2
1.3 Start-up strategy needed	4
Chapter 2 Start-up procedure descriptions	5
2.1 Heat-up process	5
2.2 Power-up process	6
Chapter 3 Model description	9
3.1 MCFC modeling	9
3.2 IC engine modeling	10
Chapter 4 Simulation	12
Chapter 5 Result and discussion	14
5.1 Stage 1 (Heat-up)	14
5.2 Stage 2 (heat-up)	17
5.3 Stage 3 (Power-up)	20
5.4 Stage 4 (Power-up)	22
5.5 Discussion	26
Chapter 6 Conclusions	27
Reference	28
Abstract	30

List of Tables

Table 1.	Start-up concept of hybrid system.....	7
Table 2.	Parameters for MCFC modeling.....	9
Table 3.	Engine geometry and operating conditions.....	11
Table 4.	Power requirement for MCFC heating.....	16
Table 5.	Simulation result of first stage.....	17
Table 6.	Simulation result of second stage.....	19

List of Figures

Figure 1.	MCFC-HCCI engine hybrid system configuration	3
Figure 2.	Start-up schedule for Li/Na electrolyte	8
Figure 3.	Simulation plan for power-up	12
Figure 4.	Schematic for first stage	14
Figure 5.	Configuration of first stage	15
Figure 6.	Schematic for second stage	18
Figure 7.	Configuration of second stage	19
Figure 8.	Schematic for third stage	20
Figure 9.	Configuration of third stage	20
Figure 10.	Air utilization in SI engine mode during power-up	22
Figure 11.	Schematic for fourth stage	22
Figure 12.	Configuration of fourth stage	23
Figure 13.	IMEP in HCCI engine mode during power-up	24
Figure 14.	Maximum temperature of MCFC during power-up	25
Figure 15.	Operable regions of the power-up process	25

Nomenclature

c	=	Specific heat
GT	=	Gas turbine
HCCI	=	Homogeneous charge compression ignition
IC	=	Internal combustion
IGCC	=	Integrated gasification combined cycle
M	=	Mole
MCFC	=	Molten carbonate fuel cell
MGT	=	Micro gas turbine
Q	=	Heat transfer
SI	=	Spark ignition
T	=	Temperature

CHAPTER 1. INTRODUCTION

1.1 Distributed Power Generation

Of the two - central VS distributed - main power generation methods, power generation system that generates under 5 MW in small voltage level (1~35 kV) [1] is classified as distributed generation. Distributed power generation may relocate the power source at very near the site of each electric load. Therefore, it has less transmission loss and more capability dealing with unpredictable electricity demands. The technologies for distributed generation include fuel cell, reciprocating engines, micro turbines and renewable sources [1]. Compared to engines and gas turbines, fuel cells are more expensive. However, fuel cells have higher efficiency and do not emit NO_x or SO_x. Molten Carbonate Fuel Cells (MCFC) use a molten carbonate salt mixture as electrolyte; operate around 600 °C; and can use natural gas directly without external reforming process. High operating temperature leads to high efficiency and provides useful high-temperature heat for combined heat and power. Therefore, many hybrid generation systems based on MCFC have been studied.

1.2 Previous Researches

Lobachyov et al. [2] suggested an MCFC combined with Integrated Gasification Combined Cycle (ICGG) to produce 170 MW of electricity. Simulation of MCFC combined with gas turbine was performed by Lunghi et al. [3]. The bottoming cycle produces an additional 12~13% power output, resulting in net electric efficiency of 67%. Ghezel-Ayagh et al. [4] suggested two kinds of direct fuel cell and turbine hybrid systems. -1) a MCFC/gas turbine (GT) system designed to generate 40 MW; and 2) a MCFC/micro-gas turbine (MGT) system generating less than 1 MW. Recently, Kim et al. [5] suggested a novel hybrid system that combined an MCFC with a Homogeneous Charge Compression Ignition (HCCI) engine to generate 300 kW. A hybrid system combined MCFC and Organic Rankine Cycle (ORC) has been developed by Angelino et al. [6]. The MCFC-ORC hybrid system with various working fluids has higher efficiency by 10-15 % than stand-alone system.

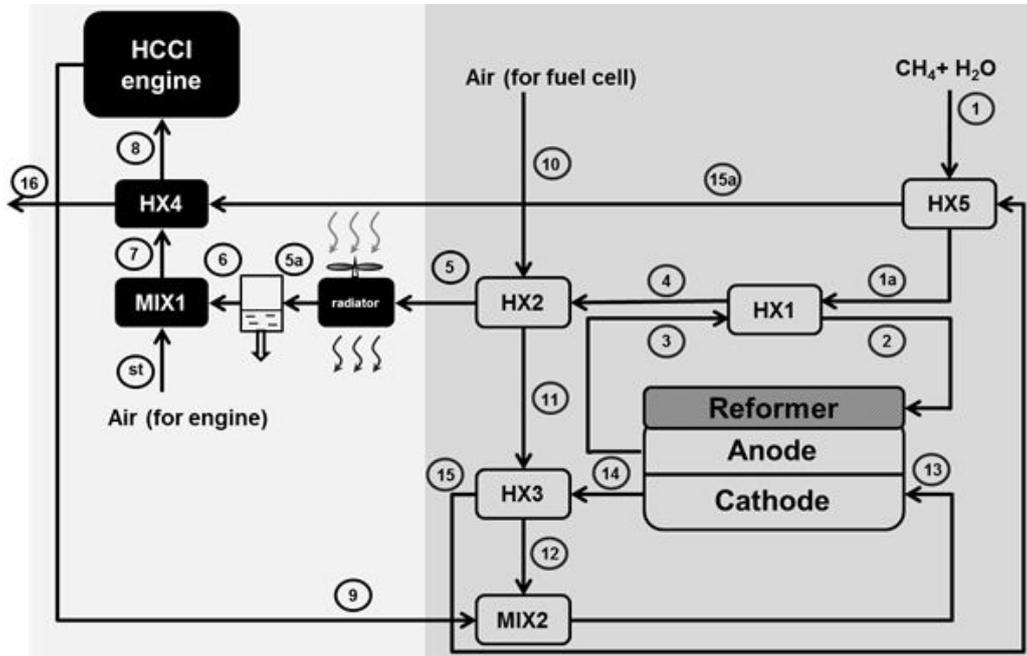


Fig. 1 MCFC-HCCI engine hybrid system configuration [5]

Fig. 1 shows the hybrid system developed by Kim et al. [5]. Methane is mixed with water in a mole ratio of 1:2.5 is preheated to operating temperature by anode off-gas and cathode off-gas. The left-over fuel in the anode off-gas is combusted in cylinder of HCCI engine replacing catalytic burner. At this time, the hybrid system can reduce carbon dioxide emission from engine exhaust gas in cathode channel. The hybrid system is about 21.2 % relative increase compared to stand-alone system by generating 55.6 kW from HCCI as well as 260 kW from MCFC engine. In their paper, analysis of the hybrid system was carried out only for the design point.

1.3 Start-up Strategy Needed

For the hybrid system to reach full load operation, MCFC has to undergo heat-up process that heating MCFC from ambient temperature to operating temperature and power-up processes that generating power from 0% to 100 % full load operation. To avoid appearing a big pore in the matrix during its sintering process, the temperature rise rate for heat-up should be slow and the total start-up process takes several hundred hours [7]. On the other hand, IC engine can be started in a few seconds. In the hybrid system, the start-up strategy using IC engine instead of the electric heater and catalytic burner is considered. To operate the IC engine during start-up process, the hybrid system needs additional control such as inlet temperature of IC engine and flow rate of stoichiometric air and additional fuel for IC engine. However, the system can maximize the use of the IC engine as back-up power generation during whole start-up process as well as heat source for heat-up process of MCFC. Therefore, the objective of the paper is to develop start-up strategies for an MCFC-IC hybrid.

CHAPTER 2. START-UP PROCEDURE

DESCRIPTIONS

2.1 Heat-up Process

Start-up of MCFC has two processes - heat-up and power-up. During the Heat-up process, the MCFC is preheated from the ambient temperature (25 °C) to the operating temperature (570 °C) without power generation. A typical heat-up process is divided into two stages - nitrogen purge stage and fuel providing stage. MCFC needs nitrogen purge in the beginning to prevent water. Nitrogen is recycled and transfers heat to the fuel cell until the cathode inlet temperature reaches 500 °C. Then, natural gas turn into hydrogen and carbon dioxide for the anode in reformer and air and carbon dioxide produced by catalytic burner for the cathode start to flow from 500 °C to the operation temperature. It is a power-up preparation stage because natural gas flows into the MCFC though the fuel utilization is zero. Typically the heat needed to preheat the MCFC is provided by electric heater. In this hybrid system IC engine replaces the electric heater and generates power in a combustion during the whole heat-up process. For this study, an SI engine has been selected since it can run at room temperature and ambient pressure unlike HCCI engine. Thus, it means that

an MCFC-IC engine hybrid system applied the SI engine does not need other auxiliaries to preheat MCFC.

2.2 Power-up Process

During the power-up process, MCFC gradually increases power generation from 0 % to 100 % by increasing the fuel flow rate and fuel utilization. In the beginning, the fuel flow rate going into anode of fuel cell and anode off-gas is relatively low compared to that of design point. An IC engine size is determined to fit the flow rate at the design point. Therefore, if the volume flow rate going into the cylinder does not fit the engine size, negative pressure of IC engine affect to MCFC operation instability.

Therefore, an IC engine needs additional fuel and stoichiometric air to increase the volume flow rate going into the cylinder and to match the engine pressure as 1 bar. Consequently, the power-up process requires additional fuel for IC engine. It means that the IC engine has to be able to burn mixture containing a small amount of inert gas because more fuel and stoichiometric air are added to the cylinder except at the design point. For this reason, HCCI engine combusting simultaneously the pre-mixture gas might not fit to the hybrid system because instantaneous combustion makes the high pressure rise rate contributing mechanical failure to cylinder. In case of SI engine, combustion using flame propagation does

not make high pressure rise rate in cylinder.

In hybrid system, as power-up process proceeds, the fuel flow rate for fuel cell and anode-off gas increases. The more inert gas goes into cylinder, the less additional fuel for engine needs. The mixture for IC engine is changed to extremely lean condition where HCCI engine is suitable. The power-up process needs two engine modes - SI mode, and HCCI mode. The switching point between the two engines or the operable range of each has to be selected MCFC-IC engine hybrid system. Thus, the whole start-up process is divided four stages - two heat-up stages and two power-up stages (Table 1) (Fig. 2).

Table 1 Start-up concept of hybrid system

Stage	Process	Power generation by MCFC	IC engine operation mode	Temperature of MCFC (°C)	Inlet gas of system
1st stage	Heat-up	No generation	SI engine	25 ~ 500	Nitrogen
2nd stage		No generation	SI engine	500 ~ 590	Fuel (0.001 kg/s)
3rd stage	Power-up	Generation	SI engine	590 ~ 600	Fuel (0.001 ~ 0.01 kg/s)
4th stage		Generation	HCCI engine	600 ~ 570	

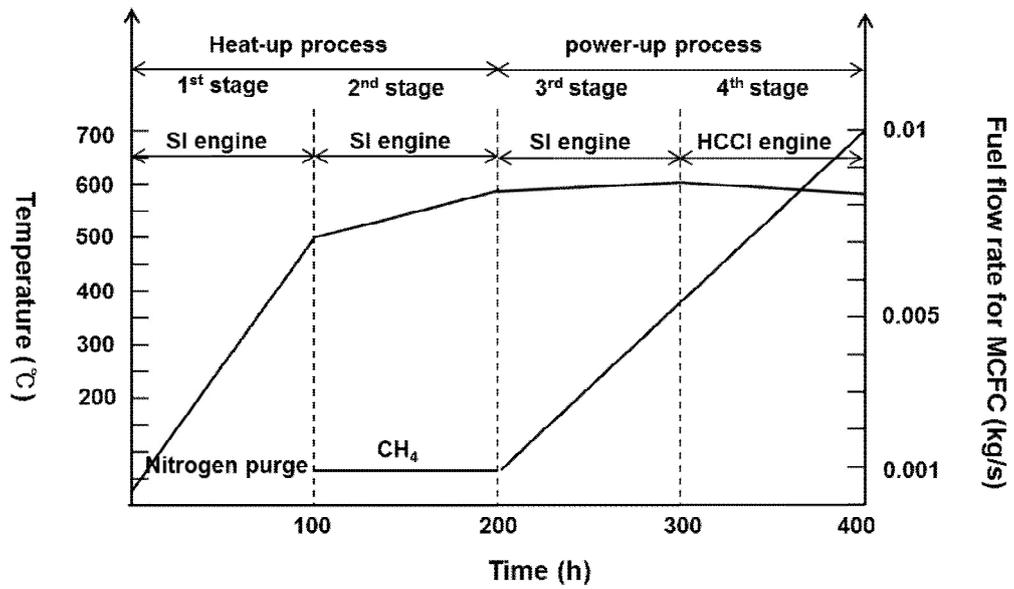


Fig. 2 Start-up schedule for Li/Na electrolyte

CHAPTER 3. MODEL DESCRIPTION

3.1 MCFC Modeling

The same MCFC modeling with previous research was referred [5]. Electrolyte of MCFC was selected Li/Na. Parallel flow of anode and cathode was assumed. The fuel cell with Li/Na as electrolyte is divided into 25 segments. Table 2 shows the parameters for MCFC modeling. Each segment consists of an isothermal phase and a non-isothermal phase. During the isothermal phase, electrochemical reactions occur. During the non-isothermal phase, the temperature of each segment is calculated from conservation of energy.

Table 2 Parameters for MCFC modeling

Parameter	Value
Electrolyte	Li/Na
Total cell area (cm ²)	10,000
Area of each segment (cm ²)	400
Segment	25

3.2 IC Engine Modeling

For IC engine modeling, MATLAB and Cantera toolbox were used to calculate the chemical reaction kinetics of the IC engine. Also, a GRI 3.0 mechanism containing 53 species and 325 reactions was selected. However, the hybrid system needs an SI engine instead of an HCCI engine during the start-up process. Therefore, an SI engine that has the same cylinder specification as the HCCI engine has been modeled as an HCCI engine with spark plugs.

To model the SI engine, an HCCI engine modeling of previous research was referred [5]. Only four-stroke - compression, ignition combustion and expansion - was applied to the SI engine. A two-zone model, which considers unburned and burned zones, has been used for combustion modeling. The combustion rate is calculated by the Wiebe function [8]. Also, methane, carbon monoxide and hydrogen was assumed that it combust and convert completely to steam and carbon dioxide in cylinder. Conventional combustion timing of SI engine is widely known to be between bTDC 25 deg ~ bTDC 5 deg [7]. Therefore, combustion timing is adapted bTDC 20 deg for SI engine modeling. Moreover, the heat transfer through the cylinder wall is calculated by the Woschni relationship. The engine geometry and operating conditions are in Table 3. Since it has the same cylinder specification as the HCCI engine, both engine modes can be obtained with one cylinder by adding spark plugs to the HCCI

engine.

Table 3 Engine geometry and operating conditions

Bore (mm)	145
Stroke (mm)	145
Cylinders	8
Displacement (L)	18.4
Compression ratio	12.5
Engine speed (rpm)	1800
Equivalence ratio	1 (Stoichiometric)

CHAPTER 4. SIMULATION

Simulation is needed to verify whether the SI engine provides sufficient heat to the MCFC during the heat-up process and to find the operable ranges for the SI and HCCI engine modes during the power-up process. Kim et al. [5] defined the design point conditions a fuel flow rate of 0.01 kg/s and a fuel utilization of 70 %. During the heat-up process, the fuel flow rate going into MCFC is assumed to be one-tenth of the full load operation, or 0.001 kg/s. For the power-up process, the fuel flow rate for MCFC is divided into intervals of 0.001 kg/s from 0.001 kg/s to that of the design point and fuel utilization is divided interval of 10 % from 20 % to that of design point. Each simulation point for the power-up process is shown Fig. 3 as dot.

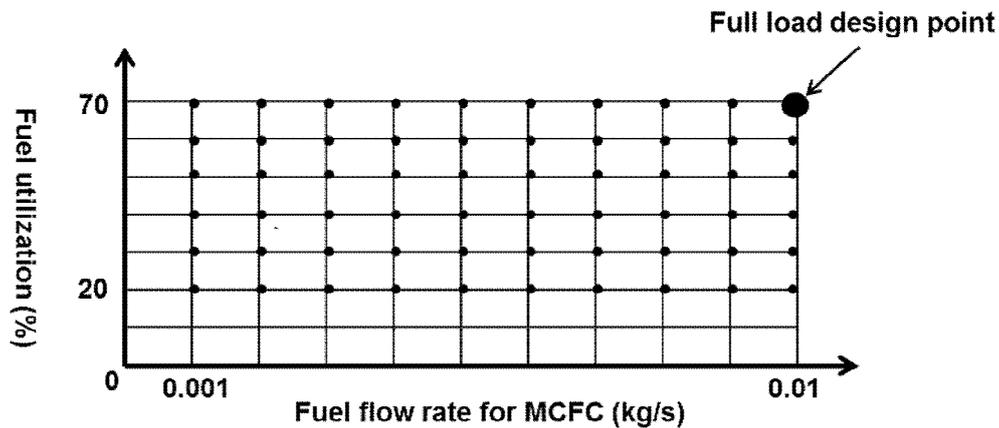


Fig. 3 Simulation plan for power-up

Moreover, each components of the hybrid system have operating limits. Following are the constraints of each component. First, the operating temperature of MCFC is restricted to 700 °C due to material constraints [9]. Oxidant utilization of MCFC is also restricted to 40 percent since the MCFC needs additional air supply than it reacts in cathode. For an HCCI engine, the Indicated Mean Effective Pressure (IMEP) is limited to 6.5 Bar. The IMEP represents steady pressure applied to the piston during expansion stroke. If the IMEP is larger than the limit, mechanical failure could occur. Finally, the effectiveness of heat exchangers is limited to 85 %. Therefore, based on the operating limit of each component, simulation for start-up strategy has been performed.

CHAPTER 5. RESULTS AND DISCUSSION

5.1 Stage 1 (Heat-up) : MCFC-SI engine (no fuel for MCFC)

Fig. 4 and Fig 5 shows the first stage operation. In this stage, the SI engine exchanges only heat with MCFC (not mass), and the SI engine has to generate sufficient heat to preheat the MCFC. The following assumptions are needed to calculate the power requirement of the MCFC.

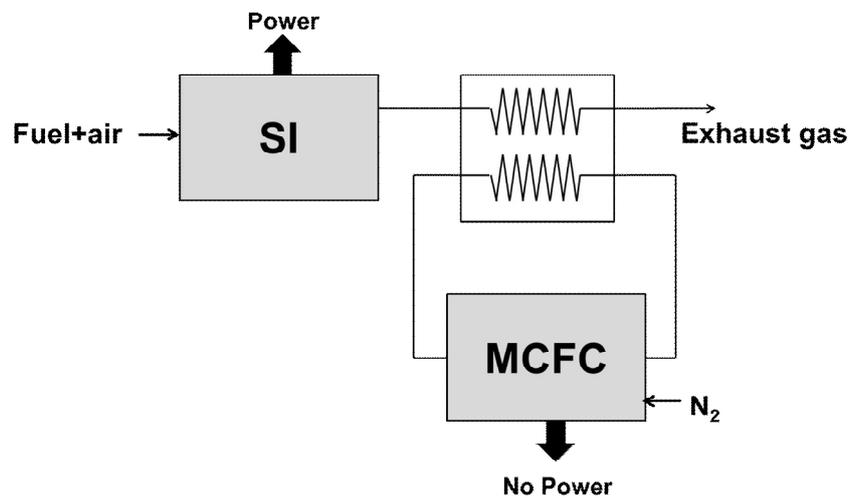


Fig. 4 Schematic for first stage

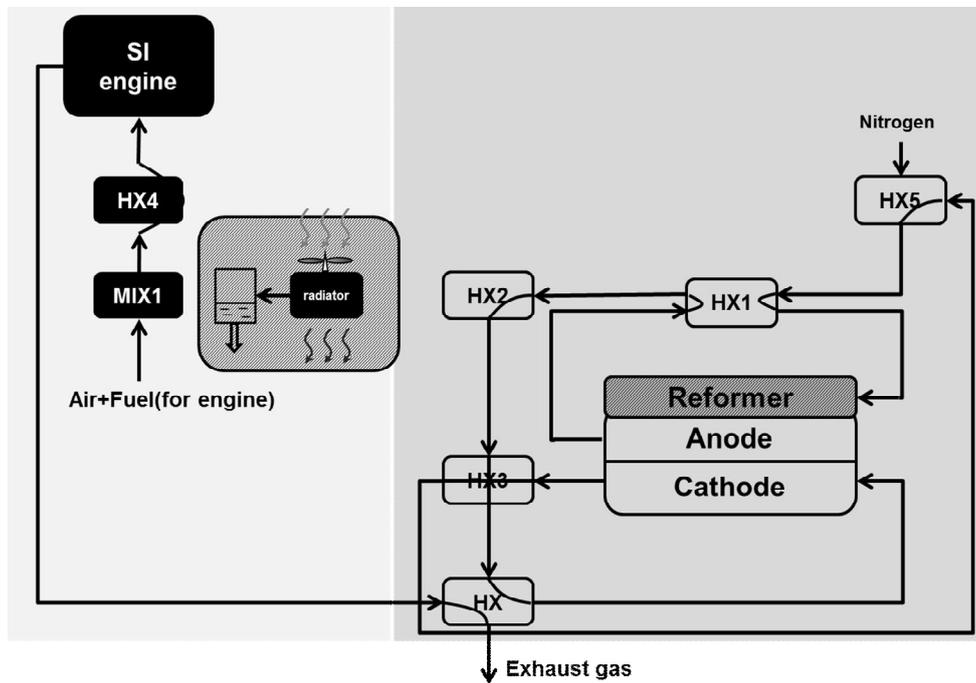


Fig. 5 Configuration of first stage

Assumptions

- 1) MCFC is filled up with only electrolyte.
- 2) MCFC electrolyte composition is 45 % of Li_2CO_3 and 55 % of Na_2CO_3 [11].
- 3) For heating, the temperature rise rate is $5\text{ }^\circ\text{C}$ per hour [10],[11].

$$Q = cm\Delta T \quad (1)$$

Table 4 Power requirement for MCFC heating. [12]

Electrolyte	Weight (kg)	Specific heat (J/kg·K)	Quantity of heat (kW)
Li ₂ CO ₃	7143	1.34	13.3
Na ₂ CO ₃	8731	0.47	5.45

This temperature rise rate (5 °C/h) is the average of the reference values [10],[11]. Table 4 shows the calculation results. To calculate the weight of each electrolyte, this research refers to DFC300 of FuelCell Energy, Inc. [12] generating 300 kW because output of MCFC on previous research is 260 kW. The weight of the fuel cell module is 15,874 kg. Thus, the weight of each electrolyte is obtained by dividing the weight of fuel cell into percentage of each electrolyte as assumed 2).

Table 5 Simulation result of first stage

Parameter	value
Fuel flow rate for engine (kg/s)	0.0170
Air flow rate (kg/s)	0.2912
Engine inlet flow rate (kg/s)	0.3082
Engine Output (kW)	350
Engine Efficiency (%)	42
Engine off-gas temperature (°C)	760

Based on Eqn. 1, the total power requirement for MCFC heating is calculated as 30.5 kW (Table. 4). Simulation results of the SI engine for first stage are in Table 5. The fuel flow rate and stoichiometric air to fill up the cylinder is respectively 0.017 kg/s and 0.2912kg/s. Since the SI engine generates 350 kW, the SI engine can preheat MCFC during first stage.

5.2 Stage 2 (Heat-up) : MCFC-SI engine (fuel for MCFC)

From second stage, the main two components start to exchange heat and mass because cathode needs carbon dioxide that the exhaust gas of SI engine (Fig. 6). As a preparation stage, fuel of one-tenth of the full load operation, or 0.001 kg/s and air is supplied to MCFC to reform. Reformed hydrogen and carbon dioxide goes into SI engine to combust

and generate power. But, if knocking occurs in SI engine, abnormally high temperature makes NO_x that has negative effect to MCFC operating. So to prevent knocking occurrence in SI engine mode, SI engine should intakes fuel gas without preheating. In other words, fourth heat exchanger of hybrid system does not work and system maintains low inlet temperature about 33 °C (Fig. 7). The heat quantity for preheating MCFC is the same as that of previous stages, 30.5 kW. Simulation results for second stage are in table 6. It shows that the SI engine generates 345 kW which is sufficient heat for MCFC heating like first stage.

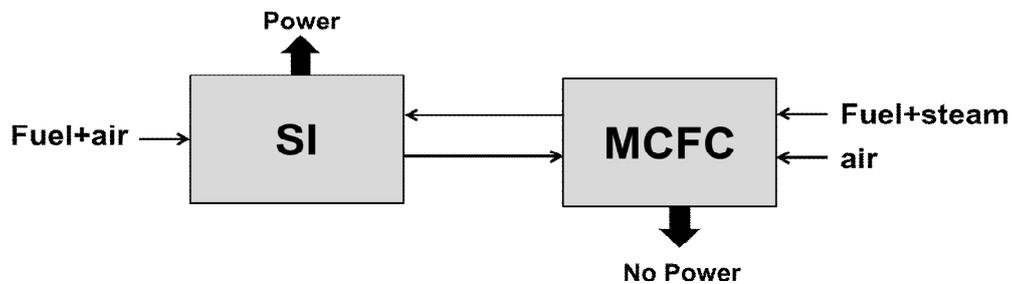


Fig. 6 Schematic for second stage

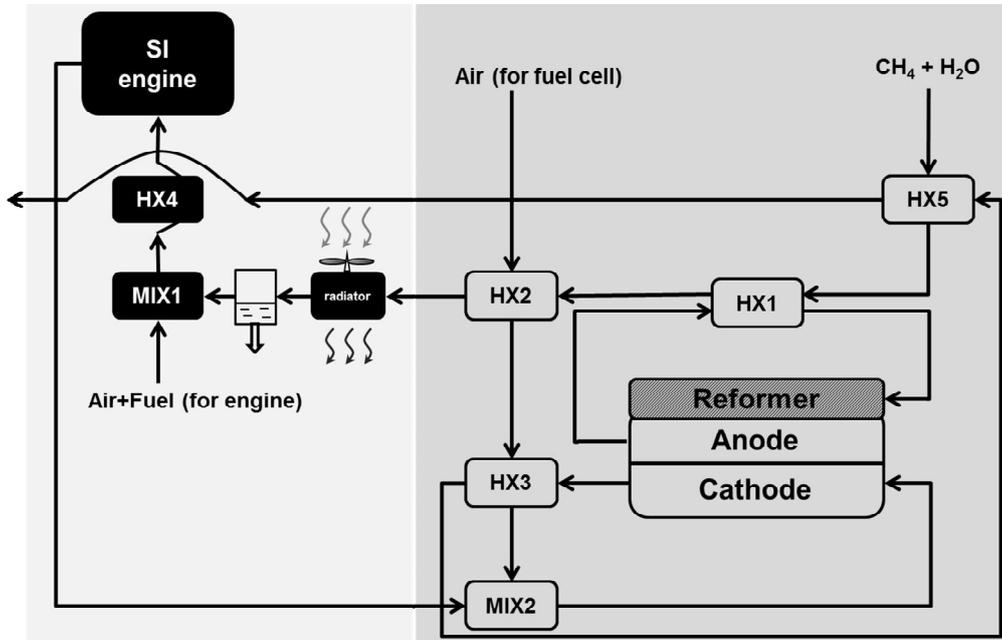


Fig. 7 Configuration of second stage

Table 6 Simulation result of second stage

Parameter	Value
Engine inlet fuel flow rate (kg/s)	0.0152
Engine Output (kW)	345
Engine Efficiency (%)	42
Engine off-gas temperature (°C)	781
Fuel flow rate for MCFC (kg/s)	0.001

5.3 Stage 3 (Power-up) : MCFC-SI engine

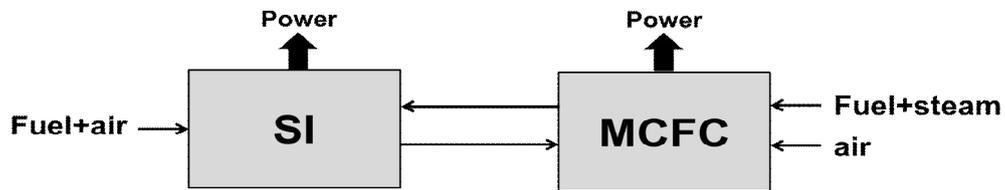


Fig. 8 Schematic for third stage

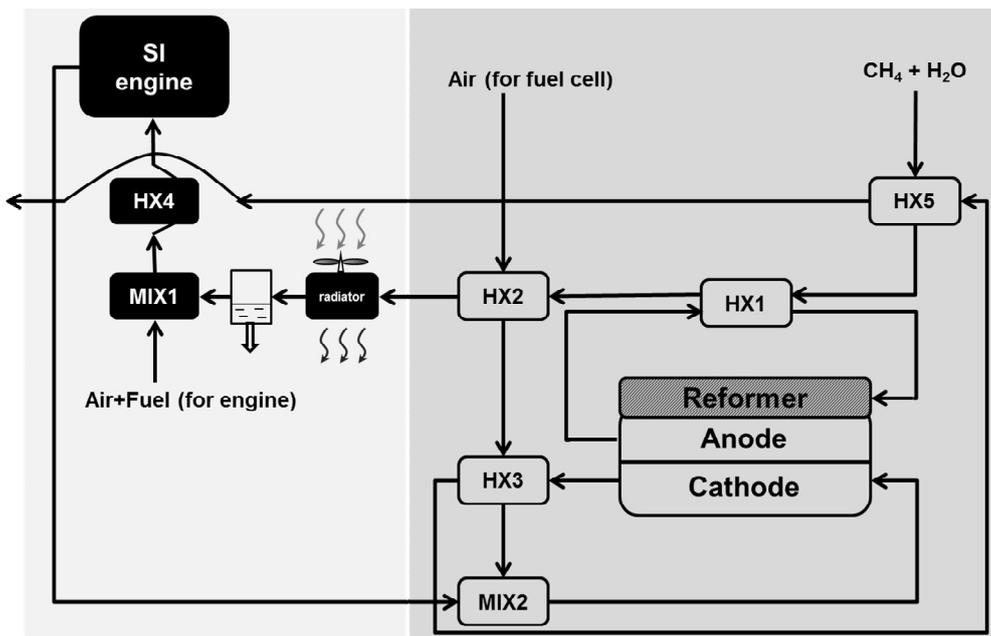


Fig. 9 Configuration of third stage

When the system reaches the power-up process, MCFC starts to generate power as well (Fig. 8). The inlet temperature of the SI engine has to be maintained at 35 °C to prevent knocking. The anode-off gas into the SI engine increase with the flow rate of fuel into the MCFC. The more anode-off gas goes into the SI engine, the less fuel and stoichiometric air are needed to fit the engine size. Also, the power and exhaust temperature of SI engine decrease. Lowered the engine exhaust temperature needs less cathode air to match the cathode inlet temperature (~600 °C). And air utilization for cathode become over the limit, 40 %. Oxidant utilization is an important factor since it restricts the operable region of the third stage. Fig. 10 shows the air utilization profile. For stable operation, the region where the air utilization is below 40 % is decided as the operable region.

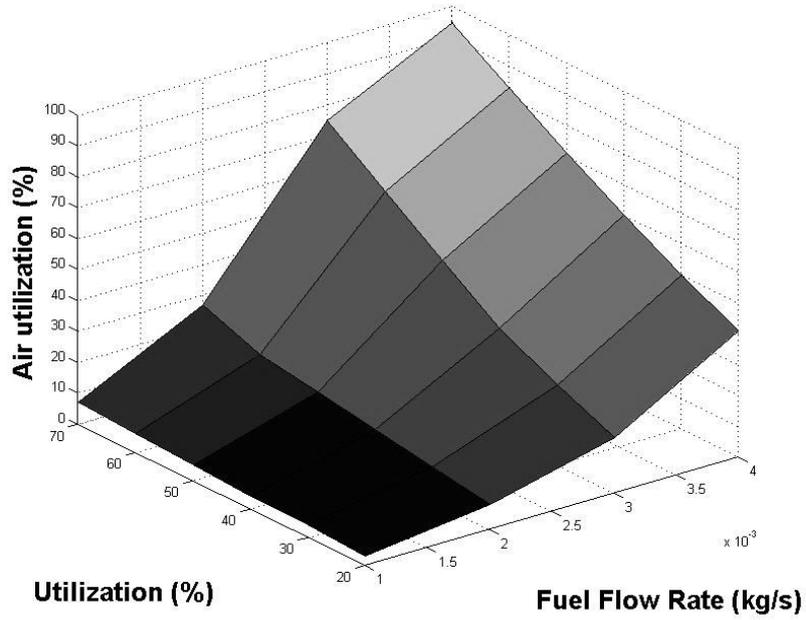


Fig. 10 Air utilization in SI engine mode during power-up

5.4 Stage 4 (Power-up) : MCFC-HCCI engine

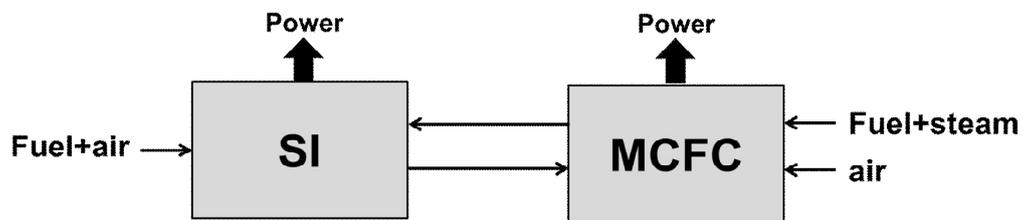


Fig. 11 Schematic for fourth stage

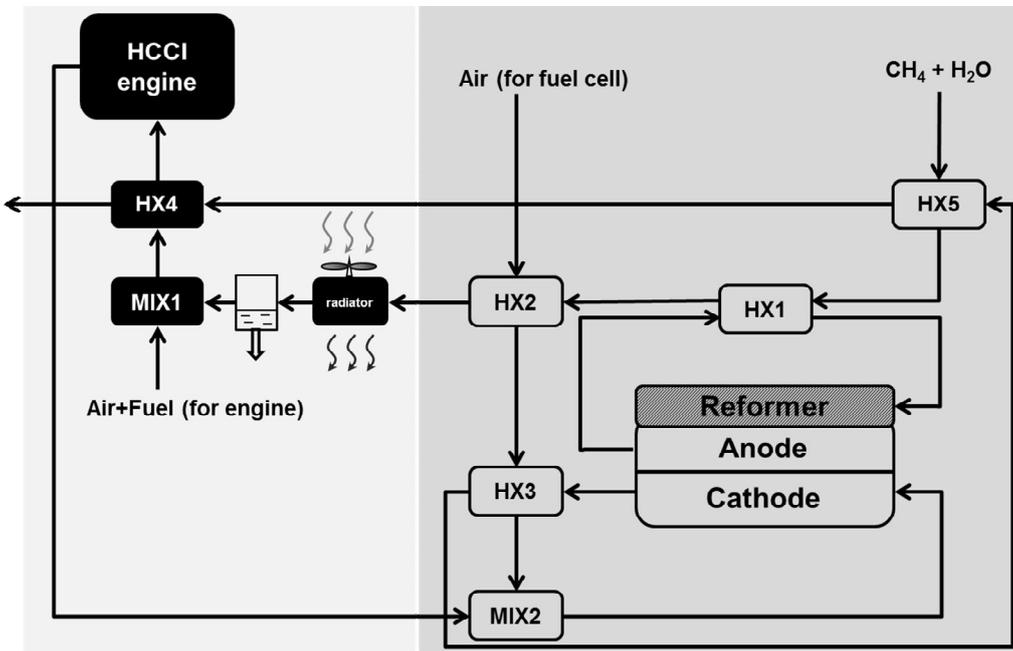


Fig. 12 Configuration of fourth stage

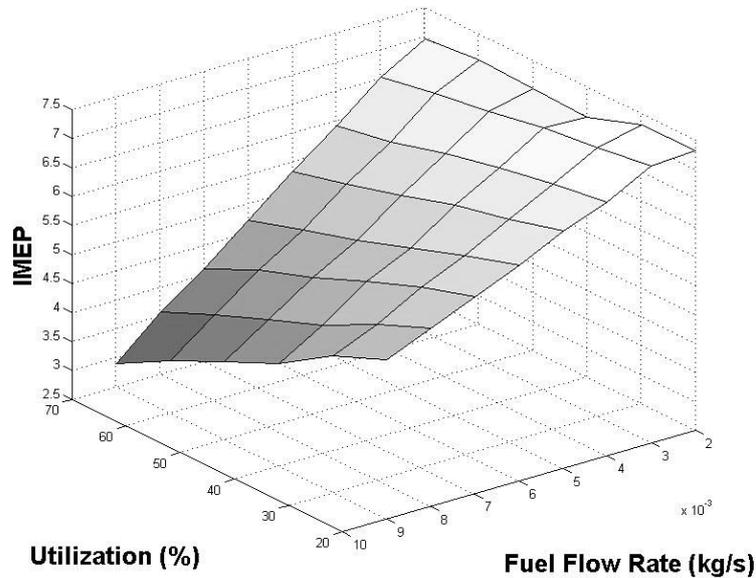


Fig. 13 IMEP in HCCI engine mode during power-up

In the stage 4, SI engine changes to HCCI engine due to operable region restriction of Stage 3 (Fig. 11) (Fig. 12). Fig. 13 shows the simulation results of IMEP for all power-up process. In the beginning of the power-up process, lower fuel utilization and lower fuel flow rate for fuel cell, IMEP is over 6.5 bar because the HCCI engine generates more power by increasing the fuel flow rate of the HCCI engine. The maximum temperature of MCFC during power-up process should be under 700 °C (Fig.14). Therefore, the operable region in Stage 4 is restricted according to the IMEP limitation of 6.5 bar and the MCFC limitation of 700 °C.

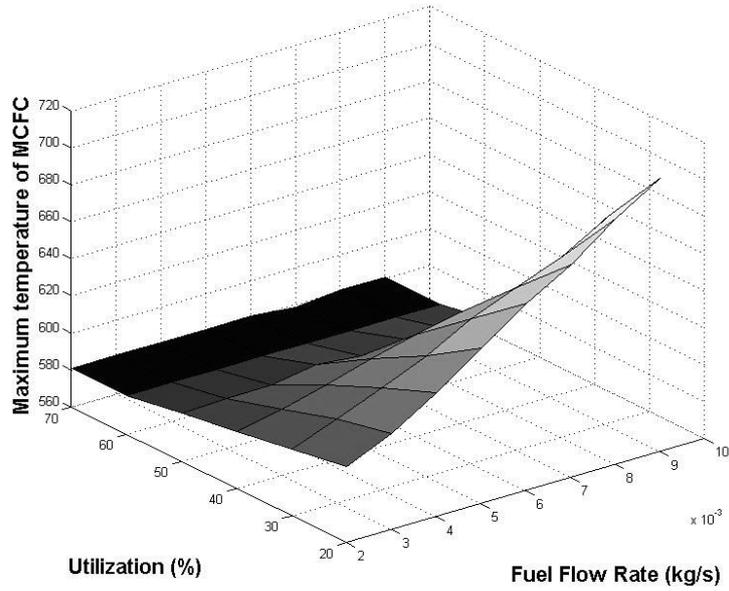


Fig. 14 Maximum temperature of MCFC during power-up

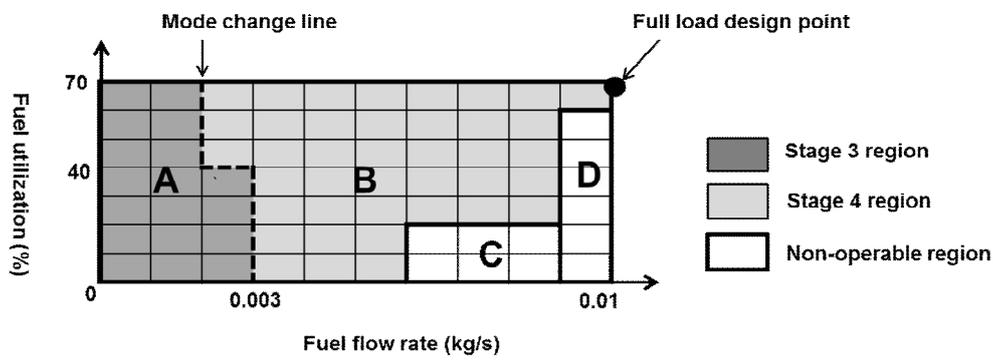


Fig. 15 Operable regions of the power-up process

5.5 discussion

The Fig. 15 shows the operable region combining the whole results during power-up process. Section A and Section B represents respectively Stage 3 (MCFC-SI engine) and Stage 4 (MCFC-HCCI engine). Operable region of both stages have been determined by simulation results based on the each constraints. In Section C, the MCFC operating temperature is higher than 700 °C. In Section D, the volume flow rate of anode off gas is larger than that required by the cylinder. Consequently, there is no overlap region where both SI engine mode and HCCI engine mode can operate. It means that switching point where engine mode is changed from SI engine to HCCI engine exist following mode change line (Fig. 15). However, when engine mode is switched, engine inlet temperature abruptly increases (33 °C to about 250 °C). To avoid mechanical shock of IC engine, inlet temperature of engine has to be increased gradually to ~250 °C, holding the fuel flow rate and fuel utilization of MCFC. Additionally, at this time IC engine could be operated spark assisted compression ignition mode. In this paper, operating scenario have not been treated. Therefore, operator can choose the highest efficiency path, the shortest path and the most generating path to fit operating situation.

CHAPTER 6. CONCLUSIONS

The starting processes of a hybrid MCFC-IC engine system, suitable for distributed power generation, have been studied. The major conclusions are as follows.

1. The start-up process has been divided into four stages - no fuel for MCFC during heating; fuel for MCFC during heat-up; MCFC-SI engine mode during power-up; and MCFC-HCCI engine mode during power-up.
2. During the heat-up process, an SI engine replaces the electric heater to generate power and to provide sufficient heat to the MCFC.
3. During the power-up process, the hybrid system has to change its engine mode from the SI engine to the HCCI engine according to its operable region.
4. The hybrid system does not need other auxiliaries to operate from the start-up to the full load.
5. The hybrid system with MCFC and IC engine is an operable and startable system.

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초 록

분산발전용 용융탄산염 연료전지와 IC 엔진의 하이브리드 시스템 시동 시나리오 개발

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본 연구는 김선엽 등[4]에 의해 개발된 Molten Carbonate Fuel Cell (MCFC)와 Internal Combustion (IC) engine 하이브리드 시스템의 시동 과정을 분석하여 하이브리드 시스템의 운전 가능성을 증명한다. 수백시간이 소요되는 MCFC의 시동 과정은 본 연구에서 2개의 heat-up 과정과 2개의 power-up 과정을 포함한 총 4개의 과정으로 나뉜다. 하이브리드 시스템 개발을 하며 새롭게 고안된 HCCI엔진을 시동 과정동안 SI엔진으로 대체함으로써 엔진의 배기열을 이용해 MCFC의 예열에 필요한 열을 제공하는 동시에 엔진부에서 추가적으로 동력을 생산할 수 있다. heat-up 과정동안 쓰이는 SI엔진은 HCCI 엔진을 개조하여 동일 실린더에서 SI엔진과 HCCI 엔진 모드가 전환 가능하도록 모델링을 하였다. 하이브리드 시스템의 heat-up 과정은 기존의 MCFC 예열 과정을 참고한다. 그 이후의 power-up 과정에는 MCFC, SI 엔진, HCCI 엔진, 열교환기의 운전 한계에 따라 Matlab을 이용한 하이브리드 시스템의 시뮬레이션 결과를 통하여 power-up 과정의 초반에는 MCFC-SI 엔진 모드로 운전하는 영역을 정의하고, 그 이후에는 switching point를 지나 MCFC-HCCI 엔진 모드 운전 영역을 구분하였다. MCFC-IC 엔진 하이브리드 시스템은 전기 히터와 촉매 연소기 없이, 시동 과정부터 디

자인포인트 운전까지 운전 가능한 시스템을 시뮬레이션 결과를 통하여 증명한다.

주요어 : 용융탄산염 연료전지, 예혼합 압축착화 엔진, 스파크 엔진;
하이브리드 시스템; 시동 전략

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