



### 공학박사학위논문

# 다공성 유로를 적용한 고분자 전해질막 연료전지의 성능에 관한 연구

### Studies on the Performance of Polymer Electrolyte Membrane Fuel Cell with Porous Flow Field

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기계항공공학부

강동균

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### 지도교수 김 민 수

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서울대학교 대학원 기계항공공학부 강 동 규

강동균의 공학박사 학위논문을 인준함

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### Abstract

# Studies on the Performance of Polymer Electrolyte Membrane Fuel Cell with Porous Flow Field

Dong Gyun Kang Department of Mechanical and Aerospace Engineering The Graduate School Seoul National University

Polymer electrolyte membrane fuel cell (PEMFC) system generates electricity by using electrochemical reactions of oxygen and hydrogen. It has been in the spotlight for many years as an alternative eco-friendly energy system because it produces only pure water as a by-product. However, there are still several challenges to apply PEMFC technology into practice. Among several challenges, it is significant to have higher performance and efficiency of the fuel cell system. In order to improve the performance of the fuel cell system, electrochemical losses should be minimized. One of the methods to reduce these electrochemical losses is re-designing the flow field in the fuel cell. Therefore, many researches about designs of flow fields in the fuel cell have been performed, and there are several types of flow fields such as parallel flow field, serpentine flow field, porous flow field, and other 3D structures.

In this study, the performance of the PEMFC with porous flow field was investigated. Metal foam flow field was used as the flow distributors in the cathode side of the fuel cell. Frist of all, performance change under various severe operating conditions for the PEMFC using metal foam flow field was scrutinized. Accelerated stress tests with and without load cycle were designed to investigate both mechanical degradation and electrochemical degradation of the fuel cell with metal foam flow field. In addition, the performance degradation of the fuel cell with conventional serpentine flow channel was examined to compare the differences between them. The performance responses of two fuel cells with serpentine flow channel and metal foam flow field were also compared under harsh operating conditions such as extremely low stoichiometric ratio and relative humidity values. The performance degradation rate of the fuel cell with metal foam flow field was slightly larger than that of the fuel cell with serpentine flow channel. However, the fuel cell with metal foam flow field showed still higher performance than that with serpentine flow channel after performance degradation. Furthermore, the fuel cell with metal foam flow field showed higher air utilization rate and better water management in low stoichiometric ratio and extremely low relative humidity, respectively.

Secondly, several different metal foam flow fields with different porosity gradients were introduced and used as flow distributors in the fuel cell. It is significant to have locally non-uniform designs in the flow field since distributions of the current density, temperature, gas, and water concentration are usually non-uniform along the flow path in the PEMFC. Therefore, non-uniform porous flow fields were designed. By evaluating and analyzing polarization curve, power curve, and electrochemical impedance spectroscopy test results, it was verified that the tailored porosity gradient in the metal foam flow field had positive effects on the performance of the fuel cell. Maximum power density of the fuel cell with proper porosity gradient in the metal foam flow field without porosity gradient. Furthermore, the performance enhancement of the fuel cell was examined in the system net power aspect, and the reasons of performance enhancement of the fuel cell with proper porosity gradient were investigated.

Lastly, other application of using the metal foam in the fuel cell field was introduced. Metal foam flow field was used as a novel way to improve the performance of the air-cooled open cathode PEMFC. Metal foam flow field was used in the cathode side of the planar unit fuel cell for the solution to conventional problems of the open cathode fuel cell such as excessive water evaporation from the membrane and poor transportation of air. Experiments were conducted, and the maximum power density of the fuel cell with metal foam increased by 25.1% compared with the conventional fuel cell without metal foam. The open cathode fuel cell with metal foam has smaller ohmic losses and concentration losses. In addition, the open cathode fuel cell with metal foam prevents excessive water evaporation and membrane drying out phenomena, and it was proven with numerical approach. Finally, the metal foam was applied to the air-cooled open cathode fuel cell stack as well as the planar unit cell. The newly designed air-cooled open cathode fuel cell stack with metal foam showed high maximum power density as much as the open cathode planar unit cell with metal foam.

Keyword: Polymer electrolyte membrane fuel cell, Porous flow field, Severe operating condition, Porosity gradient, Open cathode, Performance enhancement

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### Nomenclature

Т	temperature ((°C)
SR	stoichiometric ratio
RH	relative humidity
Р	pressure (bar)
W <sub>comp</sub>	compression work (W)
c <sub>p</sub>	specific heat (J/kg·K)
ṁ	mass flow rate (kg/s)
η	efficiency
Δ	difference operator
γ	heat capacity ratio
3	porosity
t	thickness (mm)
ū	superficial velocity (m/s)
Q	fluid flow rate (m <sup>3</sup> /s)
А	cross sectional area (m <sup>2</sup> )
u	interstitial velocity (m/s)
K	permeability (m <sup>2</sup> )
d <sub>p</sub>	pore diameter (m)
Re	Reynolds number
v	kinematic viscosity (m <sup>2</sup> /s)
dP dL	pressure gradient (kg/m <sup>2</sup> ·s <sup>2</sup> )

μ	viscosity (kg/m·s)
β	inertial coefficient (m <sup>-1</sup> )
ρ	density (kg/m <sup>3</sup> )
g	gravity (kg/s <sup>2</sup> )
Т	foam thickness (m)
W	foam width (m)
m	mass (kg)
J <sub>H2</sub> 0	mass of liquid water (kg/s·m <sup>2</sup> )
j	current density (A/m <sup>2</sup> )
F	Faraday constatnt (C/mol)
$M^{H_2O}$	molecular weight of liquid water (kg/mol)
λ	water content
$a_w$	water vapor activation
Pw	partial pressure of water vapor (Pa)
P <sub>sat</sub>	saturated pressure (Pa)
P <sup>v</sup>	vapor pressure (Pa)
K <sub>evap</sub>	Evaporation rate (1/s)
A <sub>p</sub>	pore surface area per unit volume $(m^2/m^3)$
S	liquid water saturation
R	idea gas constant (J/mol·K)
E <sub>a</sub>	activation energy of evaporation (eV)
p <sup>0</sup>	pre-exponential factor (Pa)
K <sub>B</sub>	Boltzmann constant (eV/K)
θ	contact angle (degree)

K <sub>rl</sub>	relative permeability
p <sub>c</sub>	capillary pressure (pa)
$d_{\mathrm{f}}$	diameter of finer (m)
K <sub>k</sub>	Kozeny constant

### Subscript

c	cell
ca	cathode
an	anode

### **Chapter 1. Introduction**

### 1.1 Background of the study

Polymer electrolyte membrane fuel cell (PEMFC) generates electricity by using electrochemical reactions of oxygen and hydrogen. Since it produces only pure water as a by-product, it has been renowned as an alternative eco-friendly power generation system for the future. Therefore, it has been used in many applications such as hydrogen electric vehicle, drones, residential, and industrial power generation systems. Fig. 1.1 shows how it operates.

However, even though there are many potentials, there are still some challenges needed to be solved to apply PEMFC technology into practice. There are several issues such as durability, stability, system size and performance and efficiency [1–3]. Therefore, many researchers have tried to solve these problems.

Among several challenges, it is significant to scrutinize the performance and efficiency of the fuel cell system. In order to meet the power needs of current industry, higher performance and efficiency of the fuel cell systems are required. Thus, there are many studies about minimizing electrochemical reaction losses to improve the performance of the fuel cell. As shown in Fig.

1.2, there are three electrochemical losses in the fuel cell reaction, activation loss, ohmic loss, and concentration loss. Activation losses are dominant at low current density region, ohmic losses are major voltage drops at intermediate current density region, and concentration losses mainly contributed to an overpotential at high current density region. The main reasons of activation losses are related to the rate of the interfacial oxygen reduction process, proton conductivity with the catalyst layer, and oxygen permeability limitation within the catalyst layer. Ohmic losses are highly related to the hydration of the membrane, proton conductivity, and contact area of the electrode. Lastly, concentration losses occur because of mass transport limitation due to the oxygen depletion and flooding phenomena in the flow field [4]. Among several methods to reduce these losses, re-designing the flow field in the fuel cell is one of the effective way [5]. Therefore, many researchers have investigated the flow field of the fuel cell to manage the gas diffusion and flooding phenomena in the flow field. They asserted that the type of the flow field pattern highly impacts the performance of the fuel cell [6-9]. Thus, novel 3D structured flow fields have been developed by many researchers as flow distributors in the cathode side of the PEMFC [10–13].



Fig. 1.1 Schematic diagram of electrochemical reaction of PEMFC [5]



Current density (A/cm<sup>2</sup>)

Fig. 1.2 Electrochemical losses of the fuel cell in the polarization

curve

#### **1.2 Literature survey**

#### 1.2.1 Metal foam flow field as a flow distributor in the PEMFC

A metal foam flow field is one of those 3D flow field candidates, and many researchers have used the porous metal foam as the flow field in the PEMFC. Tseng et al. [14] researched the PEMFC with metal foam as flow distributor. They used the metal foam as a flow field, and verified that PEMFC with metal foam flow field showed higher performance than the fuel cell with serpentine flow field. Shin et al. [15] also studied the effect of cell size in the metal foam flow field. They argued that there are no ribs in the metal foam flow field, and it has more enough space for gas and liquid water to flow. They also used various metal foams with different cell sizes, and scrutinized the performance difference between several metal foams with different cell sizes. Furthermore, Tsai et al. [16] investigated the effects of flow field design on the performance of the PEMFC with metal foam flow field. They showed that the convection is weak at side corners of the metal foam flow field. Thus, they used multiple inlets in order to effectively improve gas distribution in the metal foam flow field. Ting et al. [17] studied effect of operational parameters on the performance of PEMFC assembled with Au-coated nickel foam. They concerned the parameters such as cell operating temperature, cathode humidification temperature, and cathode gas stoichiometry.

In addition, some numerical analysis of the PEMFC using metal foam flow field has been conducted. Kumar and Reddy [18] conducted modeling research of PEMFC with metal foam in the flow field of the bipolar plates. They developed three-dimensional, steady-state, numerical mass transfer single cell model for PEMFC. Jo et al. [19] conducted numerical analysis for the effects of metal foam properties on flow and water distribution in the PEMFC. They used a two-phase PEMFC model, and numerically investigated the influence of metal foam porous properties and wettability on the current density distribution in the PEMFC. Jo et al. [20] also did numerical study on applicability of metal foam as flow distributor in the PEMFC. They examined the fuel cell under practical automotive operations with low humidification reaction gases. They elucidated advantages of using metal foam as flow field through multidimensional contours of flow velocity, species, and current density. In addition, Saeedan et al. [21] did numerical thermal analysis of nano-fluid flow through the cooling channels of a PEMFC filled with metal foam. Performance enhancement in the cooling system by making the temperature distribution uniform was examined.

There are several studies of using the porous metal foam in the high

temperature PEMFC. Tseng et al. [22] examined the performance of a high temperature PEMFC with metal foam as the flow field. Effects of operating temperature, stoichiometry, gas preheating temperature, and humidification on cell performance were studied. Li and Sunden [23] studied three-dimensional modeling of high temperature PEMFC with metal foams as flow distributor. They numerically investigated the cell performance and transport characteristics of high temperature PEMFC with metal foam flow field by a three-dimensional and non-isothermal model. Furthermore, Agudelo et al. [24] recently studied about the porous metal-based 3D-printed anode gas diffusion layer (GDL) for high temperature PEMFC. They used the porous thin-walled tubular elements made of 316L stainless steel as the anode GDL instead of conventional carbon-based substrates.

Some researchers used the metal foam as coolant fluid distributor in the PEMFC. Afshari et al. [25] employed a three dimensional model to simulate the fluid flow and heat transfer in cooling plates, and investigated the capabilities of different coolant flow field designs including parallel, serpentine, and metal foam.

Lastly, various studies about the metal foam flow field in the PEMFC are also conducted in recent days. Wu et al. [26] recently investigated the characterization of water management in metal foam flow field based the PEMFC using in-operando neutron radiography. This study was performed to provide clear evidence of how and where water is generated, accumulated, and removed in the metal foam flow field using in-operando neutron radiography. Weng et al. [27] researched effects of assembling method and force on the performance of PEMFC with metal foam flow field. They investigated the effects of the clamping force on the microstructures of GDL and metal foam, various resistances, pressure drops, and cell performance. Afshari [28] also recently conducted computational analysis of heat transfer in a PEMFC with metal foam flow field. A 3-D model was considered and a set of equations with electrochemical kinetics were developed and numerically solved. The author compared two fuel cells with metal foam flow field and parallel channel. In addition, Liu et al. [29] lately researched the performance improvement of PEMFC with compressed nickel foam as flow field structure. They used several nickel foams with different thicknesses, and it's operating parameters were optimized to improve the performance of PEMFC.

#### **1.2.2** Performance degradation and durability of the PEMFC

The lifetime of the PEMFC system is important to commercialize the fuel cell technology. Thus, the researches about performance degradation and durability of the fuel cell are meaningful.

There are several researches about the performance degradation and durability of the PEMFC in terms of catalyst, membrane types, operating temperature, and hydrogen crossover. Nagahara et al. [30] studied the impact of air contaminants on PEMFC performance and durability. The impact of air contaminants such as sulfur compounds and nitrogen compounds was examined in this study. Yu et al. [31] conducted in-situ analysis of performance degradation of a PEMFC under non-saturated humidification. They had a 2700 hour life test of a fuel cell with Nafion 112 membrane under non-saturated humidification. They studied the degradation mechanism with in-situ measurements of hydrogen crossover rate through the membrane and electrochemical active surface area of Pt catalyst. In addition, Wang et al. [32] conducted durability studies on the performance degradation of Pt/C catalysts of the PEMFC. The fuel cell had been operated for 2250 hour, and electrochemically active specific areas of both electrode catalysts were calculated from CV curves. The decay rate of electrochemically active specific areas of anode catalyst was much lower than that of cathode one. Yu et al. [33] also researched PtCo/C cathode catalyst for improve durability in the PEMFC. They evaluated the durability of PtCo/C cathode catalyst in a dynamic fuel cell environment, and the overall performance loss of the PtCo/C membrane was less than that of the Pt/C membrane.

There are also many researchers who investigated the performance degradation and durability of the PEMFC during fuel cell start and stop processes. Jo et al. [34] studied effects of a hydrogen and air supply procedure on the performance degradation of the PEMFC. They scrutinized effects of the procedure involving hydrogen and air supplies during the start-up process on the long-term stability. Kim et al. [35] also researched effects of cathode inlet relative humidity (RH) on PEMFC durability during startup-shutdown cycling. They showed that the performance was better for the PEMFC cycled at a lower cathode inlet RH rather than for those cycled at a higher cathode inlet RH. Furthermore, Qi et al. [36] studied saw-tooth behavior of PEMFC performance during shutdown and restart cycles. They investigated multiple reasons of sawtooth behavior such as catalyst surface oxidation state change, catalyst surface cleansing, and water management. Kannan et al. [37] also examined long term testing of start stop cycles on high temperature PEMFC stack. In this study, continuous operation and more than 1500 start stop cycles had been conducted in order to research the degradation effects of the PEMFC stack.

There are also many studies about performance degradation and durability of PEMFC using accelerated stress tests such as wet-dry cycles. Kang and Kim [38] studied membrane electrode assembly (MEA) degradation by dry/wet gas on a PEMFC. The gas injection time was 20 minutes and 5 minutes for dry gas and wet gas, respectively. They showed that the performance of the fuel cell decreased by 45.7% after 1200 wet/dry cycles. Wu et al. [39] also conducted the degradation study of Nafion/PTFE composite membrane in PEMFC under accelerated stress tests. They performed accelerated stress tests to study the degradation mechanism of the MEA with intensive RH cycling and load cycling. They could observe a long accelerated life for MEA with an edge protection and a hot-pressing process. Sharma and Andersen [40] studied catalyst degradation mechanisms during catalyst support focused accelerated stress test for PEMFCs. They compared X-ray diffraction patterns of pre-accelerated stress test and post accelerated stress test samples, and it suggested that significant change in crystallite size during potential cycling between 1.0 and 1.6 voltage. Furthermore, Schonvogel et al. [41] researched the impact of accelerated stress tests on high temperature PEMFC degradation. They used a novel load cycling test using high current densities, and compared with a test utilizing lower current densities. Accelerated stress tests were used to provoke and investigate degradation mechanisms inside commercial high temperature

proton exchange membrane electrode assemblies based on phosphoric acid doped polybenzimidazole. Petrone et al. [42] investigated accelerated stress test procedures for PEMFCs under actual load constraints. They proposed a new accelerated stress test protocol based on adaptable load cycling, and it is designed to develop a lifetime prediction model of PEMFCs. In addition, Park et al. [43] performed durability analysis of Nafion/hydrophilic pretreated PTFE membranes for PEMFCs. They evaluated the durability of a novel Nafion/poly(tetrafluoroethylene) composite membrane using an accelerated stress test. The accelerated degradation testing was performed by the wet-dry gas cycling method. They evaluated the chemical and mechanical stability of the membrane by scrutinizing the polarization curve, hydrogen crossover, and proton resistance during wet-dry cycles.

Lastly, there are various studies about performance degradation and durability of PEMFC which are conducted in recent days. Han et al. [44] recently conducted experimental analysis of performance degradation of the PEMFC stack under dynamic load cycle. This study analyzed the durability of a 3 cell short stack under dynamic load cycle conditions. The results showed that the recovery protocol could return the performance of the fuel cell at a low and a middle current density region, but it was hard to recover the performance at a very high current density region. Zheng et al. [45] also researched design of gradient cathode catalyst layer structure for mitigating Pt degradation in PEMFCs using mathematical method. They showed that larger Pt particle s near the MEA greatly mitigate the degradation of cathode. Thus, this study revealed that gradient design of particle size and Pt loading provided high durability for the PEMFC. In addition, Liu et al. [46] studied anode purge management for hydrogen utilization and stack durability improvement of PEMFC systems. They proposed an anode purge strategy, and the experimental results showed that the proposed anode purge strategy increased the hydrogen utilization rate of the PEMFC system and highly prolonged the purge interval. Garcia-Sanchez et al. [47] also lately investigated local impact of load cycling on degradation in PEMFCs. In this work, durability tests were performed using different load cycling ranges. They argued that performance losses were highly linked with inhomogeneous current density distributions.

#### 1.2.3 Air-cooled open cathode PEMFC

Air-cooled open cathode PEMFC is useful to be applied to portable devices. This is because the cathode side of that PEMFC is open, and ambient air is used for not only the consumption of oxygen, but also cooling the fuel cell stack. Thus, additional air supply and water cooling systems are not needed in order to operate the fuel cell. Since it also uses moisture in the ambient air to humidify the membrane, additional humidification system is not needed either [48]. Therefore, it only needs hydrogen supply system. This is why it is possible to be a small and compact fuel cell system, and it is a powerful candidate to be applied to portable electronic devices in the future.

However, there are still some problems needed to be solved. Air-cooled open cathode PEMFC shows relatively lower performance than the PEMFC with air supply system, humidification system and water cooling system due to poor transportation of air in the cathode side [49]. It also has some issue of water management. It is challenging that balancing water in the cathode side of the membrane because of lack of controlling ambient conditions. The membrane tends to dry out at high temperature and low humidity ambient conditions [50]. Thus, preventing from excessive water evaporation and membrane dehydration is significant, otherwise, ohmic losses would highly increase [51].

Many researchers have studied to find solutions to those problems in many different ways. Ying et al. [52] researched effects of cathode channel configurations on the performance of an air-breathing PEMFC. They optimized cathode flow field design through developing a mathematical model. Tabe et al. [53] also studied effects of cathode separator structure on performance characteristics of free breathing PEMFCs. They used two types of cathode separators, an open type with parallel rectangular open slits and a channel type with straight vertical channels with open ends. As a result, the fuel cell with open type cathode separator showed worse performance than that with channel type cathode separator. Furthermore, Zhao et al. [54] performed experimental and theoretical studies on improving the operating characteristics of an open cathode PEMFC stack by generating periodic disturbances at anode. In this study, hydrogen could be intermittently supplied from the anode outlet to the stack under the mutual cooperation of two solenoid valves, in addition to the conventional anode inlet. The results showed that the new mode could generate periodic disturbances in the anode side, which leads to the performance enhancement of the fuel cell stack. Strahl et al. [55] conducted experimental analysis of a degraded open cathode PEMFC stack. They examined the degradation mechanisms of open cathode PEMFC systems and the performance degradation of the fuel cell. They investigated and analyzed the degraded open cathode stack by means of in-situ and ex-situ methods. In addition, Silva et al. [56] researched characterization of MEA degradation for an open air cathode PEMFC. They investigated the MEA degradation during and after specified fuel cell aging testing conditions of load cycling which are related to the durability of the catalyst. Ou et al. [57] also studied performance increase for an open cathode PEMFC with humidity and temperature control. They installed bubble humidifier and fan to control the humidity and temperature. The results showed that the optimal operating conditions of relative humidity and cell temperature made the performance of the fuel cell improve. Rosa et al. [58] researched high performance PEMFC stack with open cathode at ambient pressure and temperature conditions. They considered various operating conditions such as cell temperature, air flow rate, and hydrogen pressure and flow rate. Thus, in this study, the authors investigated performance change of the fuel cell under various operating conditions, and examined how these operating conditions affected the fuel cell performance. Lopez-Sabiron et al. [59] designed and developed the cooling system of a 2 kW nominal power open cathode PEMFC stack. They developed theoretical model which included the electrochemical behavior, and the heat and mass transfer processes in order to design the cooling system of an air-forced open cathode PEMFC stack. The results could be used in the design of a dynamic and optimum cooling system. Schmitz et al. [60] scrutinized the influence of cathode opening size and wetting properties of diffusion layers on the performance of air-breathing PEMFCs. They investigated the influence of varying cathodic opening sizes (33%, 50%, and 80% opening ratios) and the influence of different wetting properties in GDLs. They used GDLs with hydrophobic and hydrophilic properties, and examined the performance change of the fuel cell.

Lastly, there are several researchers who studied about air-cooled open cathode PEMFCs in recent days. Zhao et al. [61] lately performed comprehensive anode parameter study for an open cathode PEMFC. They emphasized the importance of anode operating parameters for the performance of an air cooled open cathode PEMFC. They determined desirable anode operating parameters for the optimum fuel cell performance considering the effects of hydrogen pressure, temperature, relative humidity, and stoichiometry ratio. Zhao et al. [62] also designed optimal cathode flow channel for air cooled PEMFC with open cathode. They argued that the desirable parameters of the cathode channel are very significant factors to impact the performance of the fuel cell. In this study, several cathode channels with different width, depth, and bending were used to optimize the performance of the fuel cell and temperature distribution. In addition, Baik and Yang [63] recently developed multi-hole separators for the cathode flow channel of open cathode PEMFC. They
introduced a novel separator with a multi-hole structure for an open cathode PEMFC stack. The open cathode fuel cell stack with multi-hole structure showed better performance at high current density region, and standard deviation of the fuel cell with multi-hole separator showed more uniformity. Vichard et al. [64] also studied long term durability of open cathode PEMFC system under actual operating conditions. The purpose of this study is understanding of the degradation mechanisms of the commercial 1 kW open cathode PEMFC system. They investigated the effects of ambient temperature on the performance and degradation of the fuel cell system.

# 1.3 Objectives and scopes

The performance and efficiency of the PEMFC system are significant in order to meet the power need of current industries. Among several methods to have a higher performance of the fuel cell system, the type of flow fields in the cathode side is one of key factors. In this study, a porous metal foam flow field was used as the flow distributor in the cathode side, and the performance of the PEMFC with the metal foam flow field was investigated.

In chapter 2, performance change under various severe operating conditions for the PEMFC with metal foam flow field was examined. In several previous researches, it was verified that the PEMFC with metal foam flow field showed higher maximum power density rather than the conventional PEMFC with serpentine flow channel under normal operating conditions. However, the comparative study about durability and performance degradation of two fuel cells with metal foam flow field and serpentine flow channel does not exist. Furthermore, there were few researches about performance change under harsh operating conditions such as extremely low RH values and low stoichiometric ratio (SR) numbers for the fuel cell with metal foam flow field. Thus, this research performed substantial experimental studies in order to scrutinize the performance degradation and durability of the fuel cell with metal foam, and the performance change under various severe operating conditions.

In chapter 3, metal foam flow fields with porosity gradients in the PEMFC were studied. In general, current density, temperature, oxygen concentration, and liquid water distribution are not uniform along the flow path in the cathode side of the PEMFC. Considering these general phenomena in the flow field of the fuel cell, it is significant to make them more uniform, and finally make the performance of the fuel cell improve. Therefore, several non-uniform porous flow fields with different porosity gradients were designed. In this study, the effects of porosity gradient in the metal foam flow field on the performance of the fuel cell were investigated. In addition, the effects of porosity gradient direction in the metal foam flow field were examined, and this study verified proper porosity gradient in the metal foam could make the performance of the fuel cell enhance rather than the conventional uniform metal foam without porosity gradient.

In chapter 4, the metal foam flow field was applied to the air-cooled open cathode PEMFC. Air-cooled open cathode PEMFC has great advantages in terms of compact system size. It uses oxygen and moisture in the ambient air to supply oxygen in the cathode side and humidify the membrane. It also uses ambient air to cool down the fuel cell stack. Thus, it does not need any additional air supply system, humidification system, and cooling system. Therefore, it has high potential for a substitute of the lithium-ion battery or other secondary batteries in the future. However, it still has some problems needed to be solved such as poor oxygen transportation and poor water management on the membrane. In this research, inserting the metal foam flow field in the cathode side was introduced as a novel solution to the conventional problems of the air-cooled open cathode PEMFC. This study introduced other application of using the metal foam in the fuel cell field, and performance enhancement of the air-cooled open cathode PEMFC with inserting metal foam in the cathode side was examined.

In chapter 5, a research conclusion of the study was written, and lessons learned from this study were following.

# Chapter 2. Performance change under various severe operating conditions for the PEMFC with metal foam flow field

## 2.1 Introduction

Several researches about performance of the fuel cell with metal foam flow fiend under normal operating conditions exist. However, it is hard to operate fuel cell under normal operating condition in some situations likewise extremely cold and dry weather, or fuel limitation. Therefore, even though many researchers verified that the maximum power density of the fuel cell with metal foam was higher than the fuel cell with conventional serpentine flow channel under general operating conditions, performance change and degradation of the fuel cell under various severe operating conditions are needed to be investigated.

In this chapter, performance degradation and changes under severe operating conditions for the PEMFC using metal foam flow field were experimentally studied. Two different accelerated stress tests under severe operating conditions were performed to examine the degradation of the fuel cell. The performance degradation of the fuel cell with not only metal foam flow field, but also conventional serpentine flow channel was scrutinized for the comparative studies. The performance degradation of the fuel cell was investigated after accelerated stress test cycles by evaluating the polarization curves and power curves. In addition, electrochemical impedance spectroscopy (EIS) tests were conducted to examine the electrochemical loss changes after accelerated stress tests. Furthermore, the MEA was observed from scanning electron microscopy (SEM), after the fuel cell was disassembled. Two SEM images, MEA image from the fuel cell with serpentine flow channel and MEA image from the fuel cell with metal foam flow field, were compared, and the differences between them were investigated.

Lastly, performance changes for the fuel cells under various severe operating conditions such as low SR and low RH were examined. There are various benefits to operate the fuel cells in low SR number and RH value conditions. However, the performance of the PEMFC generally decreases as SR number and RH value becomes lower. As SR number decreases, the concentration losses would become higher and flooding phenomenon negatively affects more the performance of the fuel cell [65]. Furthermore, the ohmic losses would become higher, as RH value of supplied gases decreases [66]. Thus, different performance responses of two fuel cells with using different flow fields under harsh operating conditions were investigated. This study scrutinized how the type of flow fields in the fuel cell affected the performance change under harsh operating conditions.

### 2.2 Preparation for experiment

#### 2.2.1 Experimental apparatus

A single cell of PEMFC consists of several components such as MEA, GDLs, gaskets, cathode and anode bipolar plates with flow fields, and end plates. Fig. 2.1 shows the single fuel cell which was used in this study. Fig. 2.1 shows the fuel cell with metal foam flow field in the cathode side and serpentine flow field in the anode side. The conventional fuel cell has serpentine flow fields in both cathode and anode side. Therefore, the only difference between the conventional fuel cell and the fuel cell with metal foam flow field is the type of flow field in the cathode side. The same types of the MEA, GDL, and Teflon type of gasket were used in all experiments for the proper comparison between two fuel cells with serpentine flow field and with metal foam flow field. The metal foam flow field was inserted only in the cathode side because gas depletion and flooding phenomenon are usually dominant in the cathode side rather than the anode side. Thus conventional serpentine flow field was used in the anode side. Furthermore, the active area of the fuel cell was  $25 \text{ cm}^2$  (5cm x 5cm). The MEA was composed of Nafion-211, and catalyst layer treated as 0.45 mg/cm<sup>2</sup> for both cathode and anode side. High crystalline carbon black was used for Pt/C. The GDL (Sigracet 39BC) was a non-woven carbon paper type with micro porous layer (MPL). The carbon powder in MPL was carbon black powder & PTFE 23wt%. Lastly, serpentine flow field is made from carbon. The specification of the serpentine flow field is shown in Table 2.1.

In addition, entering gases of hydrogen gas and air were supplied to the fuel cell system by controlling mass flow controllers. Both gases were 100% fully humidified through the bubblers, and RH values of supplied gases were regulated by controlling the temperature of humidifiers. The accuracy of RH values was monitored by using humidity & temperature transmitter (MHT337, Vaisala). Furthermore, the hydrogen gas with 99.999% purity was supplied to the fuel cell. The current and voltage were measured by using an electric loader (PLZ1004W, Kikusui) for the evaluation of the fuel cell performance. EIS test was also conducted by using an impedance meter (KFM2150, Kikusui). Thermocouples (T-type, Omega) were used to measure the temperature of the fuel cell, humidifiers, and entering gases. Lastly, differential pressure between the fuel cell inlet and outlet was measured by using differential pressure transmitter (DPDH0010R, Sensys). Basic schematic of the experimental setup is shown in Fig. 2.2. Lastly, Table 2.2 shows the range and accuracy of all equipment measuring in this study.



Fig. 2.1 Single fuel cell with metal foam flow field in the cathode side

<sup>[83]</sup> 



Fig. 2.2 Schematic of experimental setup

Types of channel	Serpentine flow
Parameter	channel
Channel width (mm)	1
Inlet channel depth (mm)	0.9 / 0.6
Outlet channel depth (mm)	0.9 / 0.6
Rib width (mm)	0.9

Table 2.1 Specification of serpentine flow field

Type of apparatus	Range	Accuracy
Mass flow controllers (H <sub>2</sub> )	0~1 Lpm	±0.5% Rd plus ±0.1% FS
Mass flow controllers (Air)	0~2 Lpm	±0.5% Rd plus ±0.1% FS
Humidity & temperature transmitter	0~100%	±0.3°C (at 60°C)
Thermocouples	-200~350°C	±0.3°C
Differential pressure transmitter	0~20 kPa	±0.5%
Electric loader	0~150 V 0~200 A	±(0.2% ±0.1% FS)
Impedance meter	0.0001~9.99999 Ω	±(0.3% ±0.3% FS)

# Table 2.2 Measuring range and accuracy of apparatus

#### 2.2.2 Experimental conditions

Table 2.3 shows the experimental conditions for this study. The operating temperature was fixed at 60°C, and operating pressure, SR number, and RH values were various.

Cell size of the metal foam used in this study is 800 µm, and the porosity is about 94%. Cell size means the big polygonal opening diameter in the metal foam. The metal foam was made from nickel and coated by gold with 2 µm thickness. Two hundred times magnified metal foam picture is shown in Fig. 2.3. The picture was taken by using a digital microscope (Dino-Lite, AM4113T5X). The thickness of the metal foam is 1 mm and it was inserted into the 0.9 mm depth bipolar plate of the cathode side. Therefore, as the fuel cell was assembled, the metal foam was compressed to the 0.9 mm.

Lastly, one experimental case was repeated three times, and it was verified that the data values showed reproducibility every time. The result data in the figures was the average values of three repeated tests.

Parameter	Value
T <sub>c</sub> (°C)	60
SR <sub>an</sub>	1.5
$SR_{ca}$	1.25 / 1.5 / 1.75 / 2.0
$\mathrm{RH}_{\mathrm{an}}$ (%)	non-humidified / 50%/ 100%
RH <sub>ca</sub> (%)	non-humidified / 50%/ 100%
P <sub>an</sub> (bar)	1 / 1.5 / 2
P <sub>ca</sub> (bar)	1 / 1.5 / 2

Table 2.3 Experimental conditions



Fig. 2.3 Magnified picture of the metal foam

## 2.3 Various severe operating conditions

#### 2.3.1 Accelerated stress test without load cycle

In this study, an accelerated stress test without load cycle was introduced to investigate mainly mechanical degradation of the membrane. This accelerated stress test consists of harsh operating conditions which are wet-dry cycles. 100% fully humidified wet air and wet hydrogen gas were supplied to the fuel cell for 2 minutes, and then non-humidified dry air and dry hydrogen gas were supplied to the fuel cell for another 2 minutes. Therefore, it was designed to switch often for wet-dry cycles to have mechanical degradation dominantly. The wet-dry cycles were switched every 2 minutes because 2 minute switch was judged to be proper and often enough to examine the performance degradation of the fuel cell after several trials and errors.

Before starting the test, the polarization curve and power curve were measured, and EIS tests were performed to see the initial performance of the fuel cell. Then, these wet-dry cycles had been repeated for 432 hours (18 days) in total. In addition, polarization curves and power curves were kept continuously measuring after every 144 hours (6 days) of cycles. The EIS tests were also conducted after 432 hours (18 days) of the accelerated stress test to see the difference from the initial EIS test result. The fuel cell could be impacted mechanically by the wet-dry cycles, as the membrane keeps repeating to shrink and expand because of entering wet gas and dry gas. This phenomenon induces the mechanical degradation on the membrane such as MEA tears, cracks, catalyst thinning and delamination [67–69]. This accelerated stress test was performed for the conventional fuel cell with serpentine flow field and the fuel cell with metal foam flow field in the cathode side. Then, the differences of the performance degradation between them were examined. In this test, the mass flow rate of the entering gases was fixed as much as the amount required for loading 1 A/cm<sup>2</sup> with SR of 1.5 and 2.0 for hydrogen gas and air, respectively.

#### 2.3.2 Accelerated stress test with load cycle

An accelerated stress test with load cycle was also conducted under harsh operating conditions in order to scrutinize not only mechanical degradation, but also electrochemical degradation of two fuel cells with conventional serpentine flow field and metal foam flow field. The accelerated stress test with load cycle consists of 60 minutes of open circuit voltage (OCV), and 30 minutes of load cycle. Dry gases had been supplied for both anode and cathode sides for 30 minutes, and wet gases had been supplied for another 30 minutes during 60 minutes of OCV cycle. In 30 minutes of load cycle, wet gases had been supplied for both anode and cathode side, and fuel cell had been operated for 10 minutes under 0.32 A/cm<sup>2</sup>, 0.64 A/cm<sup>2</sup>, and 0.96 A/cm<sup>2</sup>, respectively. It was designed to have the electrochemical degradation dominantly rather than the mechanical degradation.

Likewise, this accelerated stress test with load cycle had been kept repeating for 432 hours (18 days) in total. The initial performance of the fuel cell was measured by evaluating the polarization curve, power curve, and EIS test results before starting the accelerates stress test with load cycle. The performance of the fuel cell was also kept evaluating every 144 hours (6 days) of cycles. Finally, EIS test was performed again after 432 hours (18 days) of the cycles to investigate the differences from the initial EIS test result. The mass flow rate of the supplied gases was fixed as the same amount as the mass flow rate in the accelerated stress test without load cycle. This test was performed for the fuel cell with serpentine flow field and the fuel cell with metal foam flow field to compare the differences between them.

The PEMFC is generally considered to have quite long life time in the stable and normal operating conditions. Thus, investigating the performance degradation under severe operating conditions is worthwhile. In general, the durability of the fuel cell highly depends on the performance of the MEA, and the performance of the MEA usually decreases under severe operating conditions. Therefore, the performance of the fuel cell normally decreases when it exposes to the harsh conditions, and the number of exposed times to harsh conditions depends on the fuel cell users and circumstances of use of fuel cells. Thus, it is hard to compare the exact life time between standard operating conditions and harsh operating conditions. However, it is argued that wet-dry gas cycles in accelerated stress tests could match the start-stop cycles in standard life time. In real life, the membrane degradation occurs, as the membrane shrinks and expands when the fuel cell is operated to start and stop. Therefore, one time switch from wet gas to dry gas in accelerated stress tests in this study denotes one time of start of fuel cell system in real life.

#### 2.3.3 Low SR and RH operating conditions

Lastly, the experiments were conducted under low SR number and extremely low RH value to study the performance responses of the fuel cell under various severe operating conditions. As mass flow rate of air increases, power consumption of the balance of plants (BOPs) becomes higher. Thus, it is desirable to operate the fuel cell system under low SR number for the high efficiency of the system. However, as the SR number decreases, the performance of the fuel cell usually decreases [70]. Therefore, this study investigated the performance responses of the fuel cell with metal foam flow field under low operating SR number. In this study, the SR number was changed only in the cathode side because the reaction rate of oxygen reduction is far slower rather than that of hydrogen oxidation [71].

The experiments were also performed under extremely low RH operating condition. In order to humidify the entering gases, humidifiers are generally used in the PEMFC system. This is because the performance of the fuel cell becomes worse as the RH value of the entering gases decreases due to the increase of ohmic losses [72, 73]. However, the humidifier used in the fuel cell system is not small size, and it is significant to reduce the size of the PEMFC system because of the limited space of the fuel cell application such as hydrogen electric vehicle. Thus, operating the system under non-humidified condition

without any humidifier in the fuel cell system is quite tempting operating conditions. Therefore, the performance responses of the fuel cell with metal foam flow field under almost 0% relative humidity value were examined in this chapter.

#### 2.4 Results and discussion

# 2.4.1 Performance degradation of the fuel cell after accelerated stress test without load cycle

#### 2.4.1.1 Polarization curve and power curve

The performance of each fuel cell is shown in Fig. 2.4 and 2.5. Fig. 2.4 shows the performance degradation of the fuel cell with serpentine flow field, and Fig. 2.5 shows the performance degradation of the fuel cell with metal foam flow field. It was easily checked that the initial performance of the fuel cell with metal foam flow field was higher than that of the fuel cell with serpentine flow field. Furthermore, both fuel cells showed performance degradation with the accelerated stress test. Considering that the only difference between two fuel cells is the type of flow field in the cathode side, this study could investigate how the metal foam flow field did impact the durability of the fuel cell cell cell with serpentine flow field cereased by 21.0% after 432 hours (18days) of accelerated stress test without load cycle, otherwise the maximum power density of the fuel cell with metal foam flow field and flow field decreased by 30.1%. The fuel cell with metal foam flow field had bigger performance degradation



Fig. 2.4 Performance degradation of the fuel cell with serpentine after accelerated stress test without load cycle; (a) polarization curve (b) power curve



Fig. 2.5 Performance degradation of the fuel cell with metal foam after accelerated stress test without load cycle; (a) polarization curve (b) power curve

rate than that with serpentine flow field. However, the maximum power density of the fuel cell with metal foam flow field after the accelerated stress test is still higher than that of the fuel cell with serpentine flow field. The performance degradation test was stopped after 432 hours (18 days) of test cycles since it was enough to examine the differences between two fuel cells. In addition, it was judged that more accelerated stress tests were not needed on the fuel cell to investigate the performance degradation. This is because energy efficiency of the fuel cell with serpentine flow field already became too low to meet the requirement of the current fuel cell energy industries after 432 hours (18 days) of the accelerated stress test cycles.

#### 2.4.1.2 Electrochemical impedance spectroscopy (EIS)

Secondly, EIS test results are shown in Fig. 2.6 and 2.7. EIS test is a widely well-known method to investigate the electrochemical reaction losses in the fuel cell. The impedance spectra were recorded while the frequency was swept from 4,000 Hz to 1.2 Hz with 32 moving average. In addition, measuring AC current was fixed at 10% of the DC current magnitude. It was performed at 0.32 A/cm<sup>2</sup> and 0.64 A/cm<sup>2</sup> to see the factors of the performance degradation. Performance degradation represents that electrochemical losses become larger. Thus, the reasons of the bigger performance degradation rate of the fuel cell

with metal foam were investigated with EIS tests. In the Fig. 2.6 and 2.7, the intersection between x-axis and y-axis denotes the ohmic losse which represents high frequency resistance (HFR). In addition, the arc at high frequency is attributed to the charge transfer resistance which denotes the activation loss. Lastly, mass transfer resistance is represented as an arc at low frequency, and this stands for the concentration loss in the fuel cell [74]. As shown in the Fig. 2.6 and 2.7, the charge transfer resistance increased for both fuel cells with serpentine flow field and metal foam flow field after 432 hours (18 days) of accelerated stress test. On the other hand, the high frequency resistance slightly increased only for the fuel cell with metal foam flow field, while the high frequency resistance of the fuel cell with serpentine flow field did not change. The reason of this phenomenon is highly related to the cracks and tears on the MEA due to the metal foam. The MEA was more compressed by the metal foam flow field rather than the carbon serpentine flow field when the fuel cell was assembled. Furthermore, in general, high frequency resistance is not very sensitive characteristic for degradation of the PEMFC. This is because chemical degradation can cause membrane thinning that leads to not only smaller lower resistance, but lower proton conductivity, which can offset the effects each other. Furthermore, corrosion products from oxidation of the metal can have larger effect on the total resistance [68]. Therefore, the high frequency resistance slightly increased only for the fuel cell with metal foam flow field since oxidation occurred in the metal foam flow field after the accelerated stress test. Thus, the fuel cell with metal foam flow field had bigger performance degradation rate. These phenomena are covered more in SEM image comparison section later in this paper.



Fig. 2.6 Electrochemical impedance spectroscopy of the fuel cell with serpentine flow field after accelerated stress test without load cycle; (a) J=0.32 A/cm<sup>2</sup> (b) J=0.64 A/cm<sup>2</sup>



Fig. 2.7 Electrochemical impedance spectroscopy of the fuel cell with metal foam flow field after accelerated stress test without load cycle; (a) J=0.32 A/cm<sup>2</sup> (b) J=0.64 A/cm<sup>2</sup>

# 2.4.2 Performance degradation of the fuel cell after accelerated stress test with load cycle

#### 2.4.2.1 Polarization curve and power curve

The performance degradation of two fuel cells after the accelerated stress test with load cycle was shown in Fig. 2.8 and 2.9. The maximum power density of the fuel cell with serpentine flow field decreased by 11.5%, otherwise the maximum power density of the fuel cell with metal foam flow field decreased by 24.7%. Again, it was easily checked that the performance degradation rate of the fuel cell with metal foam was bigger than that with serpentine flow field. Thus, this study shows that the fuel cell with metal foam flow field had bigger electrochemical degradation rate as well as mechanical degradation rate. However, like accelerated stress test without load cycle case, the maximum power density of the fuel cell with metal foam flow field after the accelerated stress test with load cycle is still higher than that of the fuel cell with serpentine flow field.

#### 2.4.2.2 Electrochemical impedance spectroscopy (EIS)

The EIS test results are shown in Fig. 2.10 and 2.11. Again, it was performed at  $0.32 \text{ A/cm}^2$  and  $0.64 \text{ A/cm}^2$ . The initial performance is represented by the line with circle marks, and the performance after the accelerated stress



Fig. 2.8 Performance degradation of the fuel cell with serpentine flow field after accelerated stress test with load cycle;

(a) polarization curve (b) power curve



Fig. 2.9 Performance degradation of the fuel cell with metal foam flow field after accelerated stress test with load cycle;

(a) polarization curve (b) power curve

test with load cycle is represented by the line with square marks. The charge transfer resistance increased for both fuel cells, while the high frequency resistance slightly increased only for the fuel cell with metal foam flow field. These are exactly the same results as the accelerated stress test without load cycle case. The reasons of bigger electrochemical degradation rate of the fuel cell with metal foam flow field are highly related to the OCV and electric loading. OCV and electric loading induce MEA degradation by generating hydrogen peroxide, which provokes chemical decomposition of the MEA [75, 76]. As it was mentioned above, metal foam flow field makes more cracks and tears on the membrane. Thus, more gas crossover occurs through the cracks on the membrane during OCV and electric loading, which leads to generate more hydrogen peroxide [77, 78]. Furthermore, oxidation occurred in the metal foam flow field after the accelerated stress test. Hence, the electrochemical degradation rate of the fuel cell with metal foam flow field was bigger than that of the fuel cell with serpentine flow field. However, the maximum power density of the fuel cell with metal foam was still higher than that of the fuel cell with serpentine flow field after the accelerated stress test. Thus, there was no performance overlapping node between two fuel cells. The fuel cell with metal foam still had smaller Warburg impedance after the accelerated stress test compared with the conventional fuel cell. This shows why the overall performance of the fuel cell with metal foam flow field still higher than that with serpentine flow field even after the accelerated stress tests. Therefore, although the performance degradation rate is a little bit bigger for the fuel cell with metal foam flow field, it is still better use the metal foam flow field as flow distributor in the cathode side for the high performance fuel cell system rather than the serpentine flow field.



Fig. 2.10 Electrochemical impedance spectroscopy of the fuel cell with serpentine flow channel after accelerated stress test with load cycle; (a)  $J = 0.32 \text{ A/cm}^2$  (b)  $J = 0.64 \text{ A/cm}^2$


Fig. 2.11 Electrochemical impedance spectroscopy of the fuel cell with metal foam flow field after accelerated stress test with load cycle; (a)  $J = 0.32 \text{ A/cm}^2$  (b)  $J = 0.64 \text{ A/cm}^2$ 

#### 2.4.3 Scanning electron microscopy image comparison

Two SEM images of each MEA, one from the fuel cell with serpentine flow field and the other from the fuel cell with metal foam flow field, were observed. The fuel cell was disassembled after the accelerated stress test with load cycle, and the SEM images of each MEA were taken. They were taken after the GDL was taken apart from the MEA. Cathode side top views of the each MEA are shown in Fig. 2.12 and 2.13. The image of the MEA from the fuel cell with serpentine flow field is shown in the Fig. 2.12, and the image of the MEA from the fuel cell with metal foam flow field is shown in the Fig. 2.13. Each SEM image was investigated, and it was verified that there were more cracks and tears on the MEA from the fuel cell with metal foam flow field compared with the MEA from the fuel cell with serpentine flow field. This is because of the structure of the porous metal foam, and the MEA was more compressed when the fuel cell was assembled. These cracks and tears on the MEA, shown in Fig. 2.12 and 2.13, increased charge transfer resistance and high frequency resistance since they are not covered with Pt catalyst. These also induced more gas crossover phenomenon. An energy dispersive spectroscopy (EDS) test was conducted, and it could be checked that these cracks and tears on the MEA were not covered with Pt catalyst and they mainly consisted of fluorine. The test results of the EDS are also shown in Fig. 2.12 and 2.13. In

these figures, (a) is the original SEM image, and (b) shows the region with pink color where the main composition is carbon, (c) indicates the distribution of the Pt catalyst loading, and lastly (d) displays the region with green color where the main composition is fluorine. Carbon material came from the GDL, and fluorine came from the Nafion-211 composition. The area ratio of the fluorine over the entire picture area was measured for the quantitative comparison. Fluorine distributed area ratio over the entire picture area is about 5.7% in the Fig. 2.12 (d), while the fluorine distributed area ratio is about 7.9% in the Fig. 2.13 (d). Therefore, it was verified that there were more cracks which were not covered with Pt catalyst on the MEA from the fuel cell with metal foam flow field. Thus, the main reason of the bigger performance degradation of the fuel cell with metal foam flow field is because of physical and mechanical factors of the metal foam flow field. It may be adjusted by controlling the compression torque of the fuel cell for the future works. Controlling the compression torque of the fuel cell with metal foam flow field might be helpful to enhance the durability. Lower compression torque of assembling fuel cells might induce less cracks on the MEA. However, it also might lead to higher ohmic losses due to less contact area. Therefore, it is better to find out the optimized controlling torque of the fuel cell with metal foam flow field in order to have great durability as well as high maximum power density. Thus, adjusting and optimizing controlling torque of assembling the fuel cell with metal foam could be one possible solution to enhance the durability of the fuel cell.



Fig. 2.12 SEM image and EDS images of the MEA from the fuel cell with serpentine flow field; (a) SEM image (b) distribution of carbon (c) distribution of Pt catalyst (d) distribution of fluorine





Fig. 2.13 SEM image and EDS images of the MEA from the fuel cell with metal foam flow field; (a) SEM image (b) distribution of carbon (c) distribution of Pt catalyst (d) distribution of fluorine

#### 2.4.4 Performance change under low SR number and RH value

Experiments were conducted to see the effects of low cathode SR number on the performance of the fuel cells with serpentine flow field and metal foam flow field. The operating temperature was fixed at 60°C. Both anode and cathode RH values were fixed at 50% in these tests. The results are shown in Fig. 2.14 and 2.15. The performance of the fuel cell with serpentine flow field gradually decreases as the cathode SR number gradually decreases from SR number 2 to 1.25. However, the performance of the fuel cell with metal foam flow field did not decline much until cathode SR number reached 1.25. These results mean that the fuel cell with metal foam flow field has higher air utilization rate. In addition, oxygen depletion in the flow path occurred less under relatively low SR number rather than the fuel cell with serpentine flow field.

Furthermore, experiments were performed to check the effects of extremely low RH value on the performance of the fuel cell with metal foam flow field. In this test, the operating temperature was fixed at 60°C, and the SR numbers of anode side and cathode side were fixed at 1.5, and 2, respectively. Non-humidified dry hydrogen gas and dry air were supplied to the anode and cathode side for almost 0% RH value condition. In addition, the performance of the fuel cell might be too low to conduct experiment, if the fuel cell operated



Fig. 2.14 Effects of cathode stoichiometric ratio on the performance of the fuel cell with serpentine flow field; (a) polarization curve (b) power curve



Fig. 2.15 Effects of cathode stoichiometric ratio on the performance of the fuel cell with metal foam flow field; (a) polarization curve (b) power curve

under almost 0% RH value at atmospheric pressure. Thus, the experiments were conducted under not only atmospheric pressure, but higher operating pressure such as 1.5 bar and 2 bar for both anode and cathode sides. The results were interesting. The fuel cell with serpentine flow field could not operate properly with almost 0% RH value in any operating pressure conditions. Thus, the experiment could not be continued with serpentine flow field. The fuel cell with metal foam flow field showed similar results under operating pressure 1 bar and 1.5 bar. However, the fuel cell with metal foam flow field operated fairly well with almost 0% RH values for both anode and cathode side, when the operating pressure was 2 bar. The results are shown in Fig. 2.16. This figure shows the performance comparison of the fuel cell under two different operating conditions. Even though the fuel cell was operated under almost 0% RH value, as long as the operating pressure was high enough like 2 bar, the performance of the fuel cell was slightly higher than that of the fuel cell operating under 100% RH value at atmospheric pressure. These results mean that the fuel cell with metal foam flow field has a great advantage in terms of water management under extremely low RH value. This is because the porous metal foam tends to hold up and trap water droplets in pores, which has positive effects on the water management in low RH operating conditions [79, 80]. Thus, produced water by electrochemical reactions of hydrogen and oxygen in the fuel cell tends to stay

more in the flow field, when we use porous metal foam as the flow distributor in the cathode side.

Lastly, it was scrutinized why the fuel cell with metal foam flow field could operate only at high operating pressure such as 2 bar, not at atmospheric pressure and 1.5 bar under extremely low RH value. The EIS tests were conducted at different operating pressure, and it was verified that higher operating pressure induced smaller high frequency resistance (HFR) in the fuel cell. As shown in Fig. 2.17, HFR decreases as the operating pressure increases in 0.32 A/cm<sup>2</sup>, 0.64 A/cm<sup>2</sup>, and 0.96 A/cm<sup>2</sup> current densities. These showed a significant potential of developing fuel cell system without any humidifiers in order to apply the fuel cell system into the industry which requires limited space.



Fig. 2.16 Polarization curve of the fuel cell with metal foam flow field under different operating condition



Fig. 2.17 High frequency resistance (HFR) of the fuel cell with metal foam flow field at different operating pressure

# 2.5 Summary

Firstly, performance degradation of the fuel cell with metal foam flow field was studied by using the accelerated stress tests under harsh operating conditions. The fuel cell with metal foam flow field showed bigger performance degradation rate than that with serpentine flow field. It was concluded that the main reason of the bigger performance degradation rate of the fuel cell with metal foam flow field came from more cracks and tears on the MEA. Thus, more gas crossover occurred under open circuit voltage and during electric loading in the fuel cell with metal foam flow field. Then, more gas crossover induced to generate more hydrogen peroxide which leads to a chemical decomposition of the membrane. However, the fuel cell with metal foam flow field still had smaller concentration losses after the accelerated stress test compared with the serpentine flow field fuel cell. This showed why the overall performance of the fuel cell with metal foam flow field was still higher than that with serpentine flow field even after the accelerated stress tests.

Secondly, the performance responses of the fuel cell with metal foam flow field were examined under various severe operating conditions such as extremely low SR number and RH value. Finally, it was verified that the fuel cell with metal foam flow field had higher air utilization rate and advantages in terms of water management in the flow field compared with the serpentine flow field under low SR number and RH value operating conditions, respectively.

# Chapter 3. Metal foam flow field with porosity gradient in the PEMFC

### **3.1 Introduction**

In general, oxygen concentration is not uniformly distributed along the flow path from inlet to outlet in the cathode side of the PEMFC. The velocity of supplied air is higher around inlet region rather than outlet region in the flow field. In addition, the membrane tends to dry out around inlet region, while flooding phenomenon tends to occur around outlet region. Thus, current density distribution is not uniform along the flow path [81, 82]. These phenomena are shown in Fig. 3.1. Therefore, it is significant to have locally non-uniform design of the flow field in the PEMFC.

By many researchers, it was already shown that the maximum power density of the fuel cell with metal foam flow field is higher than that of the fuel cell with serpentine flow field. However, even though there are many studies about metal foam flow fields of the PEMFC, studies about the metal foam flow field with locally non-uniform design in the PEMFC do not exist.

In this chapter, metal foam flow field with porosity gradients in the cathode side of the PEMFC were investigated [83]. It is significant to have non-

uniform porosity distribution in the metal foam flow field in order to have higher air utilization rate and better water management in the flow field of the PEMFC. In this study, the porosity gradients in the metal foam flow fields were introduced to have stronger diffusion and better utilization of air in the corners of the metal foam flow field. This finally leads to performance improvement and high efficiency of the fuel cell system. Several metal foams with different porosity gradients were designed, and the performance of fuel cells with conventional metal foam flow field without porosity gradient and metal foam flow fields with different porosity gradients were compared. Furthermore, EIS tests were performed to compare the electrochemical losses of several types of fuel cells with different metal foam flow fields. By this approach, it was verified that proper porosity gradient in the metal foam flow field had positive effects on the performance of the fuel cell. Finally, the performance improvement was investigated in the system net power aspect and the factors of performance improvement of the fuel cell with proper porosity gradient were analyzed.



Fig. 3.1 Schematic diagram of the fuel cell with metal foam

#### 3.2 Porous flow field

#### 3.2.1 Metal foam

In this study, the metal foam with 800 µm cell size was used. The porosity was about 94%. The metal foam was made of nickel coated by gold. As shown in Fig. 3.2, the thickness of the metal foam was 1 mm and it was inserted into the 0.9 mm depth indentation in the bipolar plate, thus the 1 mm metal foam could be compressed to 0.9 mm thickness. The size of metal foam was 5 cm x 5 cm, therefore, it was square shape since the reaction active area of the fuel cell was 25 cm<sup>2</sup> with square shape.

Even though the fuel cell with this metal foam flow field showed high performance and efficiency, there are still some problems when the porous flow fields are used. Some critical things are the phenomena of relatively low velocity around corner sides and outlet region, and flooding around outlet region. As it was mentioned above, air flow in the cathode side is not uniformly distributed in the flow field. There are two corner sides where weak diffusion occurs, top side corner and bottom side corner. They are shown in Fig. 3.3. In these regions, the air utilization rate is lower compared with the main flow region. This phenomenon causes the non-uniform current density and temperature distribution, which leads to the low efficiency of the fuel cell system.

This problem might be a bigger challenge to overcome in case of large area metal foam flow fields. This is because non-uniform distribution of air and water concentration in the cathode flow field is more prevalent in large area flow fields rather than in small area flow field. PEMFC needs to be operated in the form of large area flow field stack to be used in the vehicles. Even though the fuel cell with metal foam flow field showed better performance and higher efficiency than the fuel cell with carbon serpentine flow field in the size of small unit cell, it is very hard to verify that it is still effective in the case of large area flow field fuel cell stacks. This is because the corner side weak gas diffusion zone becomes much bigger in case of the large area metal foam. To solve this problem, Tsai et al. [16] made separate metal foam regions by using multiple inlets and tried to achieve stronger convection at the corners. Although this is an interesting approach and effective in the size of the small unit cell, it is not easy to apply this technology to large area flow field fuel cell stacks. This is because it is difficult to design multiple air inlets in the fuel cell stack. Thus, this solution could not solve the intrinsic problem of the metal foam flow field when it need to be used in large area fuel cell stacks.

Therefore, the aim of this study is to design non-uniform porous flow field,

which can be applied to conventional large area fuel cell stack. A novel approach was attempted, namely, introducing a porosity gradient in the metal foam flow field.



Fig. 3.2 Cathode bipolar plate with metal foam flow field [83]



Fig. 3.3 Bottom side corner and top side corner in the metal foam flow Field [83]

#### 3.2.2 Metal foam with porosity gradient

Several types of inclined bipolar plates were designed and manufactured specially for the metal foam with porosity gradient. Inclined bipolar plates mean the bipolar plates with gradual change of the depth of the pocket from inlet to outlet. Exactly the same metal foam was used, but inclined bipolar plates with the inclined depth in the pockets were designed. Thus, the level of compression of the metal foam could change when the metal foam was inserted into the inclined bipolar plates and compressed by assembling the fuel cell. This process could change the porosity gradient in the metal foam flow field. As the depth of the pocket in the bipolar plate becomes smaller, the porosity of the metal foam becomes lower.

However, when the fuel cell was assembled, not only the metal foam was compressed, but also the GDL was compressed. Therefore, the level of compression of the GDL becomes also different, when the level of compression of the metal foam becomes different by using different inclined bipolar plates. The different level of compression of the GDL also might affect the performance of the fuel cell. Thus, two different experiments were conducted to see how different level of compression of the GDL affected the performance of the fuel cell. In the first case, 1 mm thickness metal foam was compressed in the pocket of the bipolar plate with the GDL together when the fuel cell was assembled. In the second case, 1 mm thickness metal foam was compressed in the pocket of the bipolar plate in advance, and then the fuel cell was assembled with the GDL. Consequentially, two cases did not show much differences on the final performance of the fuel cell. Thus, the effects of different level of compression of the GDL was neglected in this study.

Fig. 3.4 shows the six types of the porous flow fields with different porosity gradients. Type 1 is the conventional metal foam which has uniform porosity distribution. In case of type 2, the porosity of the metal foam decreases gradually along diagonal direction from gas inlet to outlet. In case of type 3, it is exactly the same as the type 2, except for the slope of the porosity gradient. In case of type 3, the porosity of the metal foam decreases with steeper slope compared with the type 2. In case of type 4, the porosity of the metal foam increases along the diagonal direction from gas inlet to outlet. Other two types, type 5 and 6, are different from type 3 and 4 in that they have different directions for the porosity gradient in the metal foam flow field. Even though they have the same slope for porosity gradient as the type 3 and 4, the porosity of the metal foam decreases along the diagonal parallel direction from left to right and vertical direction from top to bottom in the type 5 and 6, respectively. Table 3.1 shows the specifications of each flow field.



Fig. 3.4 Several types of metal foam flow fields with different porosity

Gradients [83]

	Type 1	Type 2	Type 3	Type 4	Type 5	Type 6
type	Metal foam without porosity gradient	Metal foam with porosity gradient				
Inlet pocket depth in bipolar plate (mm)	0.9	0.9	0.9	0.5	0.9	0.9
Outlet pocket depth in bipolar plate (mm)	0.9	0.7	0.5	0.9	0.5	0.5
Direction of the porosity gradient	None	Diagonal	Diagonal	Diagonal	Horizontal	Vertical

Table 3.1 Specification of flow fields [83]

## 3.3 Preparation for experiment

#### **3.3.1 Experimental conditions**

Experimental conditions for this study are shown in Table 3.2. The operating temperature was fixed at 60°C and all experiments were operated at atmospheric pressure. The stoichiometric number was 2 and 1.5 for the cathode and anode side, respectively. In addition, both entering gases were 100% fully humidified through the humidifiers.

Lastly, the type of the bipolar plates was only changed to examine the effects of porosity gradient in the porous flow field on the performance of the fuel cell.

Parameter	Value
T <sub>c</sub> (°C)	60
SR <sub>an</sub>	1.5
SR <sub>ca</sub>	2.0
$RH_{an}$ (%)	100
RH <sub>ca</sub> (%)	100

 Table 3.2 Experimental conditions [83]

#### 3.4 Results and discussion

#### 3.4.1 The effect of the porosity gradient in the metal foam flow field

#### **3.4.1.1** Polarization curve and power curve

The experiments were conducted to investigate the effect of the porosity gradient in the metal foam flow field. The results are shown in Fig. 3.5. These results show that the porosity gradient in the metal foam flow field has considerable effects on the performance of the fuel cell. Steeper porosity gradient in the metal foam flow field showed better performance since the fuel cell with bipolar plate with 0.9 mm - 0.5 mm depth gradation shows higher performance than the fuel cell with 0.9 mm - 0.7 mm depth gradation in the bipolar plate. Furthermore, decreasing the porosity gradually along the diagonal direction from inlet to outlet is more effective for the higher performance of the fuel cell than increasing the porosity gradually along the diagonal direction from inlet to outlet. This means that the performance of the fuel cell enhanced with tailored porosity gradient in the metal foam not just because average porosity values of the metal foam became lower. Type 3 and type 4 have exactly the same average porosity values in the metal foam flow field, but they showed different performance results. Type 3 showed higher maximum power density than type 4. Therefore, performance of type 3 fuel cell became higher and the reason for that is not just the lower average porosity values. Thus, the proper porosity gradient in the metal foam flow field had positive effects on the fuel cell performance. These phenomena can be seen in the power curve as well. Type 3 showed the highest maximum power density and the maximum power density increased by 8.23% compared with the type 1 which is the conventional metal foam flow field without porosity gradient. These are because of nonuniform design of the flow field with porosity gradient in the metal foam flow field. The gas tends to flow more easily to the direction of high porosity region because the permeability in the porous media increases as the porosity value increases [84, 85]. Thus, proper porosity gradient in the porous flow field makes a force for the gas to flow more to the side corners of the flow field. Hence, the porosity gradient along the diagonal direction from inlet to outlet was made, and the gas tends to flow more to the corners in the metal foam, not directly flow to the direction of the outlet. Thus, steeper porosity gradient makes stronger diffusion and flow velocity becomes higher in the side corners of the metal foam flow field. This improves the performance of the fuel cell. The reasons for the performance improvement of the fuel cell with porosity gradient in the porous flow field are covered in more detail later in this chapter.



Fig. 3.5 Polarization curve and power curve of different types of fuel cells referring to Table 3.1 for descriptions [83]

#### 3.4.1.2 Electrochemical impedance spectroscopy (EIS)

Fig. 3.6 shows the results of EIS measurements. The EIS tests were performed at  $0.32 \text{ A/cm}^2$  and  $0.64 \text{ A/cm}^2$  to verify the assertion that the fuel cell with porosity gradient in the metal foam flow field has smaller losses than the fuel cell with metal foam flow field without porosity gradient. The impedance spectra were recorded while the frequency was swept from 1,260 Hz – 0.4 Hz with 32 moving average. The measuring AC current was fixed at 10% of the DC current magnitude. As shown in Fig. 3.6, the arc size of type 3 is the smallest one compared with the other types in both 0.32 A/cm<sup>2</sup> and 0.64 A/cm<sup>2</sup> cases, which means that the electrochemical losses of type 3 are the smallest among them. This is because stronger diffusion occurs in the side corners of the metal foam flow field and well distributed flow causes uniformly distributed current density and temperature in case of type 3.



Fig. 3.6 Electrochemical impedance spectroscopy of fuel cells with different porosity gradient; (a) J = 0.32 A/cm<sup>2</sup> (b) J = 0.64 A/cm<sup>2</sup> [83]

# **3.4.2** The effect of the porosity gradient direction in the metal foam flow field

#### 3.4.2.1 Polarization curve and power curve

Another experiments were performed to examine the effect of the porosity gradient direction in the metal foam flow field. In case of type 3, the porosity gradient was made along the diagonal direction from inlet to outlet. In order to study the effect of the porosity gradient direction in the metal foam flow field on the performance of the fuel cell, the type 5 and 6 were made. In case of type 5, there is a porosity gradient along horizontal direction from left side to right side. In case of type 6, there is a porosity gradient along vertical direction from top to bottom. Then, the experiments were conducted to see the performance differences between them. The results are shown in Fig. 3.7. Type 3 still shows the highest maximum power of the fuel cell in this experiment as well. This is because type 3 could make a stronger diffusion in both side corners of the metal foam, top side corner and bottom side corner. On the other hand, type 5 or type 6 can make a stronger diffusion only in one side corner of the metal foam, bottom side corner or top side corner, respectively. To be more specific, type 5 is designed to have relatively high porosity region only in bottom side corner while top side corner becomes relatively low porosity region. In addition, type 6 is designed to have relatively high porosity region only in top side corner while bottom side corner becomes relatively low porosity region. Therefore, this experimental result means that metal foam flow field with porosity gradient along the diagonal direction has the tailored flow pattern in the flow field, which causes uniform current density in the fuel cell. This is because type 3 is designed to have relatively high porosity region in both top and bottom side corners. Besides, type 6 shows the worst performance among them since water droplets and films are stuck in the bottom side corner due to the gravity effect. In case of type 3 and type 5, porosity gradient forces the entering gas to flow more into the bottom side corner and purge more water than type 6. In addition, this result double checked that the reason for the higher performance of the fuel cell of type 3 is not just the lower average porosity values in the metal foam, and it is not because the metal foam was more compressed, which reduces the contact resistance. The average porosity values in the metal foams of type 3, type 5, and type 6 are exactly the same and all of them were compressed with the same amount. Therefore, porosity gradient direction in the metal foam flow field impacts the performance of the fuel cell and it is significant to have proper porosity gradient direction in the metal foam flow field.

#### **3.4.2.2 Electrochemical impedance spectroscopy (EIS)**

The EIS tests were conducted again in the same way as above to compare


Fig. 3.7 Polarization curve and power curve of fuel cells with different porosity gradient directions referring to Table 3.1 for descriptions [83]

the electrochemical reaction losses at both 0.32 A/cm<sup>2</sup> and 0.64 A/cm<sup>2</sup> cases. As shown in Fig. 3.8, type 3 shows the smallest electrochemical losses among them which exactly matches to the result of the polarization curve and power curve. In addition, the arc size of the type 6, triangular mark in the figure, is bigger than the other type of the fuel cells. Specifically, the intersection values between kinetic loop and resistance axis at high frequency are almost the same for the type 3, 5, and 6. This is because all of them have the same average porosity values in the metal foam and they were compressed with the same amount. However, the sizes of the arcs of each fuel cell are different. This result verified that proper porosity gradient direction in the metal foam flow field reduces the concentration losses of the fuel cell because of more active gas diffusion in the corner sides of the metal foam flow field. Thus, the fuel cell of type 3 has the smallest electrochemical reaction losses and shows the best performance among them.



Fig. 3.8 Electrochemical impedance spectroscopy of fuel cells with different porosity gradient directions; (a) J = 0.32 A/cm<sup>2</sup> (b) J = 0.64 A/cm<sup>2</sup> [83]

#### 3.4.3 Performance improvement in the system net power aspect

The differential pressures were measured in different current density regions for the fuel cell of type 1 and type 3. Type 3 shows the best performance, therefore, differential pressure tests were performed to see whether there was a bigger differential pressure in case of the type 3 rather than the type 1. Since higher differential pressure causes more flow work in the balance of plant, the differential pressure of the metal foam flow field with porosity gradient should be checked. Results are shown in Fig. 3.9. Even though there are some differences between two differential pressure values, it hardly checks the difference in low current density region. The gap between two values becomes bigger in high current density region. However, the biggest difference between two values is only 1.48 kPa even in high current density region, and this value is not big enough to bring more flow work of BOPs and offsets the power improvement of the fuel cell with porosity gradient in the metal foam flow field. By using Eq. (1), the additional flow work could be calculated caused from extra 1.48 kPa differential pressure in the fuel cell system [86]. Eq. (1) is obviously a very useful general equation. In this case, the value for air of specific heat ( $C_p$ ) is 1004 J/kg·K and heat capacity ratio ( $\gamma$ ) is 1.4. Furthermore, the efficiency of the compressor is 0.9. Consequently, additional differential pressure of 1.48 kPa brings about 0.03 W flow work of BOPs, and

the value is not big enough compared with the maximum power improvement due to the proper porosity gradient in the metal foam flow field.

$$W_{\text{comp}} = c_p \frac{T_c}{\eta_{\text{comp}}} \left[ \left( \frac{P + \Delta P}{P} \right)^{\frac{\gamma - 1}{\gamma}} - 1 \right] \dot{m}$$
(1)



Fig. 3.9 Differential pressure of fuel cells in the cathode side [83]

# 3.4.4 Reasons of the performance improvement with proper porosity gradient in the metal foam flow field

It was shown that the proper porosity gradient in the metal foam flow field had positive effects on the performance of the fuel cell. In the experimental results, type 3 shows the best performance among them. In this section, the reasons of the performance enhancement of the type 3 are investigated. In order to specifically scrutinize the effects of porosity gradient of the type 3, the other experiments were conducted. In this experiment, 20 cm<sup>2</sup> (2 cm x 10 cm) area of rectangle shape metal foams were used. These experimental conditions are the same as the previous experiments. The schematics of the metal foams are shown in Fig. 3.10. These metal foams were used in order to minimize the weak diffusion effects in the side corners which were mentioned in the section of 3.2.1 metal foam. Thus, in this experiment, weak diffusion zones in the metal foam were minimized, and only the porosity gradient effect itself could be examined. Since the type 3 showed the best performance in the previous experiments, the porosity gradient of type 3 was used in this section. In Fig. 3.10, type 1 is the conventional metal foam flow field without porosity gradient, and type 2 is the metal foam flow field with porosity gradient from inlet to outlet.

The experimental results are shown in Fig. 3.11. Type 2 shows the higher



Fig. 3.10 Two types of metal foam flow fields with different porosity gradient



Fig. 3. 11 Polarization curve and power curve of two fuel cells without porosity gradient and with porosity gradient

maximum power density than the type 1. The maximum power density of the type 2 increased by 6.8% compared with the type 1. Therefore, it was verified that the proper porosity gradient in the metal foam flow field made the performance of the fuel cell improve even in different shape of the metal foam.

The reasons of the performance enhancement could be explained with structure variation of the metal foam flow field. In case of type 2, the thickness of the metal foam flow field changed from 0.9 mm to 0.5 mm along the flow path. It is shown in Fig. 3.12. Then, by using Eq. (2), the porosity values could be calculated, as the thickness of the metal foam changed [87].

$$\varepsilon = [t - t_{init} \times (1 - \varepsilon_{init})]/t$$
<sup>(2)</sup>

In Eq. (2), t is the thickness (mm) of the metal foam,  $t_{init}$  is the initial thickness (mm) of the metal foam, and  $\varepsilon_{init}$  is the initial porosity value of the metal foam. Fig. 3.13 shows the porosity distribution of two types of the fuel cells. Type 1 shows the metal foam with uniform porosity distribution, and type 2 shows the metal foam with porosity distribution. Porosity values gradually decreased along the flow path from inlet to outlet. This porosity change makes huge difference for the performance of the fuel cell. By using Eq. (3) and (4), interstitial velocity of the entering gas in the metal foam flow field could be calculated [88].

$$\bar{\mathbf{u}} = \frac{\mathbf{Q}}{\mathbf{A}} \tag{3}$$







0.9 0.8 0.7 0.6	6 0.5
-----------------	-------



Fig. 3.12 Thickness distribution in the metal foam flow field; (a) type 1

(b) type 2











Fig. 3.13 Porosity distribution in the metal foam flow field; (a) Type 1

(b) Type 2

$$\mathbf{u} = \frac{\overline{\mathbf{u}}}{\varepsilon} \tag{4}$$

In Eq. (3),  $\bar{u}$  is the superficial velocity (m/s), Q is the fluid flow rate (m<sup>3</sup>/s), and A is the cross sectional area (m<sup>2</sup>). In Eq. (4), u is the interstitial velocity (m/s) and  $\varepsilon$  is the porosity value. As the porosity value decreases in the metal foam flow field, interstitial velocity of the entering gas increases. It is shown in Fig. 3.14. In this case, it was assumed that the mass flow rate of the entering gas was about 1 liter per minute, which is in the normal range for the mass flow rate when the single fuel cell is operated. In general, the flow velocity of entering gas decreases along the flow path from inlet to outlet in the flow field of the fuel cell. Thus, as the porosity value gradually decreases along the metal foam flow path from inlet to outlet, higher velocity profile could be developed around outlet region compared with the conventional metal foam flow field without porosity gradient.

In addition, pore sizes of the metal foams were experimentally measured in different thicknesses of the metal foams. The results are shown in Fig. 3.15 and 3.16. The digital microscope (Dino-Lite, AM4113T5X) was used for measuring the pore sizes. As shown in the Fig. 3. 15, the pictures of the metal foams were taken as the thickness of metal foams changed from 0.9 mm to 0.5 mm. Then, the average values of the pore sizes were calculated for each metal foam thickness case. Finally, the pore size distribution in the metal foam of type



Fig. 3.14 Porosity and interstitial velocity at different positions





0.9 mm thickness

0.8 mm thickness



0.7 mm thickness



0.6 mm thickness



0.5 mm thickness

Fig. 3.15 Pore size of the metal foam flow field in different thickness

[83]







Pore size (mm)



Fig. 3.16 Pore size distribution in the metal foam flow field; (a) type 1

(b) type 2

2 could be shown in Fig. 3.16. As the thickness of the metal foam decreases, the pore size of the metal foam also decreases. With these measured pore size values, permeability could be calculated by using Eq. (5) [21].

$$K = \frac{d_p^2 \cdot \varepsilon^3}{150 \cdot (1-\varepsilon)^2}$$
(5)

In Eq. (5), K is the permeability  $(m^2)$ ,  $d_p$  is the pore diameter (m), and  $\epsilon$  is the porosity value. The results are shown in Fig. 3.17. As the porosity value gradually decreases along the metal foam flow path from inlet to outlet, the permeability values also decreases. In other words, permeability value becomes smaller, as the porosity value becomes smaller.

Then, Reynolds number could be calculated by using Eq. (6) [89].

$$\operatorname{Re} = \frac{u \cdot d_p}{v} \ge 1 \tag{6}$$

In Eq. (6), u is the velocity (m/s),  $d_p$  is the pore diameter(m), and v is the kinematic viscosity (m<sup>2</sup>/s). The results are shown in Fig. 3.18. All Reynolds numbers at all positions in the metal foam flow field are bigger than 12 and smaller than 16. Thus, All Reynolds numbers are bigger than 1, and finally Forchheimer equation could be used. It is shown in Eq. (7) [90].

$$\frac{\mathrm{dP}}{\mathrm{dL}} = \frac{\mu}{\mathrm{K}} \mathrm{u} + \beta \rho \mathrm{u}^2 \tag{7}$$

In Eq. (7),  $\mu$  is the viscosity (kg/m·s), u is the velocity (m/s), K is the permeability (m<sup>2</sup>),  $\beta$  is the inertial coefficient (m<sup>-1</sup>), and  $\rho$  is the density







Fig. 3.17 Permeability values at different positions



Fig. 3.18 Reynolds numbers at different positions

 $(kg/m^3)$ . Forchheimer equation is generally used to account for pressure gradients across the foams. Pressure gradients are highly related to the viscous term and inertia term in the porous media. In Eq. (7), the left term on the right hand side denotes viscous term, and the right term on the right hand side stands for inertia term. As the permeability value becomes smaller around outlet region of the metal foam flow field due to the porosity gradient, the pressure drops increase around outlet region. In addition, as the velocity increases around outlet region of the metal foam flow field due to the porosity gradient, the pressure drops also increase around outlet region. Therefore, the metal foam flow field with proper porosity gradient could have higher differential pressure around outlet region compared with the conventional metal foam which is the type 1. This phenomenon is also described in Fig. 3.19. The metal foam flow field of the type 2 could have higher differential pressure around outlet region compared with inlet region. Thus, it could remove the liquid water well around outlet region. To be more specific, it could be explained with capillary pressure by using Eq. (8) [91].

Capillary pressure = 
$$\frac{g}{TW\epsilon} \cdot m + \frac{\mu}{K\epsilon(TW\rho)^2} \cdot m \cdot \frac{dm}{dt} + \frac{1}{\rho(\epsilon TW)^2}$$
  
 $\frac{d}{dt}(m \cdot \dot{m}) + \frac{\mu \dot{m}_e(W+T)}{K\rho^3(TW)^3\epsilon^2} \cdot m^2$  (8)

The first term on the right hand side is the hydrostatic pressure, the second



Fig. 3. 19 Pressure gradients across the metal foam of type 2

term on the right hand side is the viscous term, and the third term is the inertia term. The last term on the right hand side is the evaporation term which acts as an extra pressure drop term. In this study, the last term could be neglected since flooding phenomena occurs in the metal foam flow field rather than evaporation from the foam surface. In Eq. (8), g is the gravity  $(m/s^2)$ , T is the foam thickness (m), W is the foam width (m), K is the permeability (m<sup>2</sup>),  $\varepsilon$  is the porosity,  $\rho$  is the density (kg/m<sup>3</sup>),  $\mu$  is the viscosity (kg/m·s), m is the mass (kg), and m is the mass flow rate (kg/s). As mentioned above, the metal foam flow field of the type 2 was designed to have smaller porosity and pore size around outlet region. Thus, smaller permeability values and larger velocity values around outlet region could make both viscous term and inertia term increase. Finally, as shown in Eq. (8), higher viscous term and inertia term could make the capillary pressure become higher. In other words, the metal foam flow field of the type 2 could have higher capillary pressure around outlet region compared with the conventional metal foam flow field of the type 1, which leads to remove liquid water well around outlet region. These are the reasons of the performance enhancement of the fuel cell with proper porosity gradient in the metal foam flow field.

# 3.5 Summary

In this chapter, several different metal foam flow fields with different porosity gradients in the PEMFC were investigated. Several performance tests, EIS tests, and differential pressure tests were conducted, and it was found that proper porosity gradient in the metal foam flow field improved the performance of the fuel cell. It was shown that the metal foam flow field with porosity gradient along the diagonal direction from inlet to outlet had positive effects on the performance of the fuel cell. The maximum power density of the fuel cell with type 3 increased by 8.23% compared with the fuel cell with conventional metal foam flow field without porosity gradient. In addition, the performance enhancement was investigated in the system net power aspect. Lastly, it was explained why the fuel cell had higher performance with proper porosity gradient in the metal foam flow field by interpreting the relations of thickness, porosity, permeability, pore size, flow velocity, and capillary pressure in the metal foam flow field.

# Chapter 4. Performance enhancement of aircooled open cathode PEMFC with inserting metal foam in the cathode side

# 4.1 Introduction

The PEMFC is the type of fuel cells which can be operated at relatively low temperature. Thus, it has many applications such as hydrogen electric vehicle and residential power generation. It has a great potential to substitute conventional secondary batteries in the future.

Especially, air-cooled open cathode PEMFC is in the limelight because need of power and energy of electronic device increases. Air-cooled open cathode PEMFC is useful to be applied in portable devices. As it was mentioned above, it is possible to be a small and compact fuel cell system, and it is a powerful candidate to be applied to portable electronic devices.

However, there are still some problems for the air-cooled open cathode PEMFC. The performance of the air-cooled open cathode PEMFC is relatively lower compared with the PEMFC with air supply, humidification, and water cooling system. This is because of poor transportation of air in the cathode side, and some issue of water management [49]. It is difficult to balance water in the cathode side of the MEA due to lack of controlling ambient conditions. The MEA drying out phenomenon occurs at high temperature and low humidity ambient conditions [50]. Thus, it is important to prevent excessive water evaporation and MEA dehydration phenomena.

The metal foam flow field was used in the general PEMFC in previous studies. In this chapter, for a better application of using metal foam in the fuel cell field, a porous flow field is designed and used for the innovative solution to conventional problems of the air-cooled open cathode PEMFC [92].

The metal foam was inserted in the cathode side of the open cathode fuel cell in order to have strong air diffusion in the flow field. The open cathode fuel cell with metal foam in the cathode side could have a large contact area as well as strong air diffusion to the MEA side. It could also prevent excessive water evaporation and membrane dehydration, which leads to overall performance enhancement of the open cathode fuel cell. Experiments were conducted with open cathode planar unit cell in several different cases to verify the assumptions. Furthermore, numerical approach was performed to interpret the reasons of performance improvement of the open cathode fuel cell stack of 5 cells was designed and manufactured by inserting the metal foam in the cathode side. Eventually, it was proved that the suggested solution of inserting metal foam in the cathode side worked very nicely in the air-cooled open cathode fuel cell stack as well as the air-cooled open cathode planar unit fuel cell.

## 4.2 Preparation for experiment

#### 4.2.1 Metal foam

In this study, a metal foam with 1200 µm cell size was used for the porous flow field in the cathode side, and it's porosity was about 94%. The metal foam was made of nickel and coated by gold with 2 µm thickness. It is shown in Fig. 4.1 (a) with 200 times magnified picture. In addition, Fig. 4.1 (b) shows the three-dimensional picture of the metal foam with gas diffusion directions. Air could diffuse to any direction including through-plane direction and in-plane direction in the porous metal foam flow field. To be more specific, throughplane direction in the metal foam means the direction with green color arrows in the figure, and in-plane direction means the direction with red color arrows and blue color arrows. In other words, gas could diffuse to all three directions in the porous metal foam. Thus, porous metal foam is different from the conventional GDL of the fuel cell in that gas could mainly diffuse to throughplane direction in the conventional GDL. A schematic picture of open cathode planar unit fuel cell using metal foam in the cathode side is shown in Fig. 4.2.



(a)



**(b)** 

Fig. 4.1 Pictures of the metal foam; (a) magnified picture of the metal foam (b) three-dimensional picture with gas diffusion directions [92]



Fig. 4.2 A schematic picture of the open cathode planar unit fuel cell with metal foam [92]

#### 4.2.2 Experimental apparatus

In this study, air supply system, humidification system, and water cooling system were not used since ambient air was used to supply air to the open cathode fuel cell by a fan (EF-70BM, Hanil). The moisture in the ambient air was used to humidify the MEA and the fuel cell was also cooled with ambient air. The hydrogen gas was supplied to the fuel cell with mass flow controllers with non-humidified condition. The purity of hydrogen gas was 99.999%.

The experiments were conducted not only for the open cathode fuel cell with metal foam in the cathode side, but for the open cathode fuel cell without metal foam in order to compare the performance between them. For the proper comparison, the same type of MEA, GDL, and gaskets were used in all experiments. In addition, the serpentine flow channel was used as a flow distributor in the anode side. The active area of the fuel cell was 25 cm<sup>2</sup> for both the open cathode planar unit cell and the open cathode fuel cell stack. Table 4.1 shows the specification of the serpentine flow channel used in the anode side

Table 4.1 Specification of serpentine flow field for open cathode PEMFC

[92]	
Types of ch Parameter	annel Serpentine flow channel
Channel width (mm)	1
Inlet channel depth (mm)	0.4
Outlet channel depth (mm)	0.4
Rib width (mm)	0.9

#### 4.2.3 Experimental conditions

The temperatures of ambient air, entering hydrogen gas, and fuel cell were controlled. The temperatures of ambient air and entering hydrogen gas were fixed at 21°C. It was judged that conducting the experiments at 21°C is suitable because open cathode fuel cell system should be operated in an ambient temperature condition. The temperature of the fuel cell was controlled and fixed at 40°C for the planar open cathode unit cell. This is because the temperature of the unit cell rose up to 40°C by itself due to the generated heat from electrochemical reactions when the air-cooled open cathode fuel cell was operated. Since additional heaters are not normally used in the air-cooled open cathode fuel cell system, 40°C temperature of fuel cell was appropriate for this study. In addition, the RH value of hydrogen gas was almost 0% since nonhumidified hydrogen gas was supplied. The RH value of ambient air was fixed at about 10% because air-cooled open cathode fuel cell generally shows a low performance in low RH condition [50]. Thus, scrutinizing the performance of open cathode fuel cell at low RH values of ambient air is very significant. All experimental conditions are shown in Table 4.2 including air mass flow rate of the fan, and SR number for the anode side. Excessive air was supplied constantly by using fan since the variable of this experiment was type of flow fields in the cathode side, not air mass flow rate. It was judged that constant air

mass flow rate is needed in this research for the proper comparison between two different fuel cells with metal foam and without metal foam in the cathode side. Thus, air mass flow rate was fixed for the right performance comparison between the open cathode fuel cells with metal foam and the conventional open cathode fuel cell without metal foam. Lastly, it should be noted that the experiments were conducted at atmospheric pressure.

Parameter	Value
Temperature of the ambient air (K)	294
Temperature of the entering hydrogen gas (K)	294
Temperature of the cell (K)	313
Stoichiometric ratio number <sub>an</sub>	1.5
Air mass flow rate of fan (m <sup>3</sup> / min)	11.9
Relative humidity <sub>an</sub> (%)	non-humidified
Pressure <sub>an</sub> (bar)	1
Pressure <sub>ca</sub> (bar)	1

# Table 4.2 Experimental conditions [92]

### 4.3 Results and Discussion

#### 4.3.1 Planar unit fuel cell

#### **4.3.1.1** Polarization curve and power curve

Experiments were conducted to compare performance of two open cathode fuel cells without metal foam and with metal foam in the cathode side. Two current collectors with open area of 52% and 70% were used in the cathode side. The results are shown in Fig. 4.3. The open cathode fuel cell with metal foam showed much higher performance in both current collectors with open area of 52% and 70%. Fig. 4.3 (b) shows the power curve, where the performance of the conventional open cathode fuel cell with 70% open area was too low when compared with that of the open cathode fuel cell with metal foam. In case of the current collector with 52% open area, the maximum power density of the open cathode fuel cell with metal foam increased by 25.1% compared with conventional open cathode fuel cell. This is a huge performance enhancement. It was verified that inserting the metal foam in the cathode side of the open cathode fuel cell could be a novel solution to conventional problems of open cathode fuel cells. In conventional open cathode fuel cell without metal



Fig. 4.3 Performance of the open cathode fuel cells without metal foam and with metal foam; (a) polarization curve (b) power curve [92]
foam, as open area of the cathode side becomes larger, ohmic loss increases due to smaller contact area and excessive water evaporation from the membrane. On the other hand, as open area becomes smaller, ohmic loss decreases, however, electrochemical reaction area decreases. Therefore, mass transport problem occurs, and concentration losses increase [93]. By this reason, it is a big challenge to overcome these problems. However, as the metal foam was inserted in the cathode side between the GDL and the current collectors with 52% open area and 70% open area, the problems could be solved. Adding metal foam in front of the GDL could prevent excessive water evaporation and MEA drying out phenomena. Liquid water droplets tends to be held and trapped in pores of the porous metal foam [79, 80], and it has positive effects on the performance of the open cathode fuel cell. This assertion will be covered with more detailed descriptions in the numerical approach section of this paper.

#### **4.3.1.2 Electrochemical impedance spectroscopy (EIS)**

The EIS test was performed to investigate the causes of performance enhancement of the open cathode fuel cell with metal foam. The EIS test was conducted at current density of 0.32 A/cm<sup>2</sup> and 0.64 A/cm<sup>2</sup>. The impedance spectra was recorded while the frequency was swept from 3160 Hz to 1.2 Hz with 32 moving average. Measuring AC current was fixed at 10% of the DC current magnitude. The results are shown in Fig. 4.4. It could be verified that the open cathode fuel cell with metal foam had much lower HFR rather than the conventional open cathode fuel cell. This is because the open cathode fuel cell with metal foam can have large contact area due to the structure of the porous metal foam. It could be also verified that the additional porous metal foam beside GDL could prevent excessive water evaporation phenomenon through the EIS test. This is because lower ohmic losses also mean wellhydrated membrane of the fuel cell. In addition, the open cathode fuel cell with metal foam also showed smaller concentration losses as well as ohmic losses. The sizes of arcs in low frequency range are smaller for the open cathode fuel cell with metal foam in both current densities of  $0.32 \text{ A/cm}^2$  and  $0.64 \text{ A/cm}^2$ . The porous metal foam was inserted between the GDL and cathode current collector as shown in Fig. 4.2. Therefore, it could make more flow field space for air diffusion behind ribs of the current collector. On the other hand, the conventional open cathode fuel cell has 52% open area or 70% open area, thus the open cathode fuel cell with porous metal foam flow field can have larger open area than the conventional open cathode fuel cell due to more porous flow field space for air diffusion behind ribs of the current collector. By this reason, the open cathode fuel cell with porous metal foam could solve mass transport problem in relatively high current density region. In conclusion, the open cathode fuel cell with metal foam can have not only lower ohmic losses due to larger contact area and more water retention, but also lower concentration losses because of more porous flow field space for air diffusion between GDL and cathode current collector.



Fig. 4.4 Electrochemical impedance spectroscopy of the open cathode fuel cells without metal foam and with metal foam; (a) J = 0.32 $A/cm^2$  (b)  $J = 0.64 A/cm^2$  [92]

#### 4.3.2 Numerical approach

#### 4.3.2.1 Numerical approach for liquid water saturation profile

Numerical approach was conducted to compare the liquid water saturation distribution through MPL, GDBL, and the porous metal foam between two open cathode fuel cells without metal foam and with metal foam. Fig. 4.5 shows the modeling domain for this study. Only liquid water was considered, thus condensation of water vapor was not considered. It was also assumed that liquid water flux existed only in xdirection. In addition, liquid water was assumed to be fully evaporated at the outer surface of porous media in x-axis. Furthermore, steady-state is assumed, and the water flux driven by electroosmotic drag is assumed to be equal to the water flux by back diffusion in a steady state. The numerical approach was conducted to verify the assertion that the open cathode fuel cell with metal foam could prevent excessive water evaporation from the membrane. Eq. (9) shows governing equation for liquid water saturation [5].

 $J_{H_2O, \text{ gen}} + J_{H_2O, \text{ drag}} - J_{H_2O, \text{ back diffusion}} = J_{H_2O, \text{ evap}} + J_{H_2O, \text{diff}}$ (9)

In Eq. (9),  $J_{H_2O, gen}$  means liquid water formation at cathode catalyst layer (CCL).  $J_{H_2O, drag}$  denotes liquid water flux in the membrane from anode side to cathode side due to electroosmotic drag.  $J_{H_2O, back diffusion}$  refers to



Fig. 4.5 Modeling domain for liquid water saturation in porous media
[92]

liquid water flux in the membrane from cathode side to anode side because of back diffusion. It happens when liquid water accumulates a lot in the cathode side compared with the anode side.  $J_{H_2O, evap}$  is amount of liquid water which evaporates, and  $J_{H_2O,diff}$  is amount of liquid water which diffuses out through the porous media. However, liquid water flux in the membrane by the electroosmotic drag is balanced by the back diffusion in this study [94]. In a real situation, back diffusion truly happen when liquid water accumulates a lot on the membrane in the cathode side, but liquid water on the membrane tends to evaporate in the air-cooled open cathode fuel cell. In addition, as nonhumidified hydrogen gas was used in the anode side, water content in the membrane is quite small. Therefore, it is quite reasonable to neglect the liquid water flux by electroosmotic drag and back diffusion in the open cathode fuel cell. Considering this analysis, Eq. (9) can be re-written by Eq. (10). Then,  $J_{H_2O, gen}$  can be formulated by Eq. (11) [5].

$$J_{H_2O, \text{ gen}} = J_{H_2O, \text{ evap}} + J_{H_2O, \text{diff}}$$
(10)

$$J_{H_2O,gen} = \frac{j}{2F} M^{H_2O}$$
(11)

$$\lambda = 0.0043 + 17.81a_{\rm w} - 39.85a_{\rm w}^2 + 36a_{\rm w}^3$$
 for  $0 < a_{\rm w} \le 1$  (12)

$$a_{w} = \frac{P_{w}}{P_{SAT}}$$
(13)

j is the current density (A/m<sup>2</sup>), F is a Faraday constant (c/mol), and  $M^{H_2O}$ 

is a molecular weight of water (kg/mol). In addition,  $\lambda$  implies a water content.  $a_w$  is a water vapor activation, and it can be calculated by partial pressure of water vapor (P<sub>w</sub>) over saturated pressure at system operating temperature (P<sub>SAT</sub>). With Eq. (12) and Eq. (13), it could be verified that water content is quite low in these conditions because non-humidified gas was used in the anode side, and the relative humidity of ambient air was set to be 10% in this study.

The amount of liquid water which evaporates could be calculated in the porous media by using Eq. (14) [95, 96].

$$J_{H_2O,evap} = K_{evap} \cdot \frac{1}{A_p} \cdot s \cdot \frac{M_{H_2O}}{RT} (P^{SAT} - P^v)$$
$$= K_{evap} \cdot \frac{1}{A_p} \cdot s \cdot \frac{M_{H_2O}}{RT} \cdot \left\{ \left( p^0 \cdot e^{\left(\frac{-E_a}{k_B \cdot T}\right)} \right) - P^v \right\}$$
(14)

 $K_{evap}$  is an evaporation rate constant (1/s),  $A_p$  is a pore surface area per unit volume (m<sup>2</sup>/m<sup>3</sup>), and s is liquid water saturation. T is a temperature (K) and R is an idea gas constant (J/ mol·K).  $E_a$  is an activation energy of evaporation (eV) and  $k_B$  is a Boltzmann constant (eV/K). In addition, p<sup>0</sup> is a preexponential factor and P<sup>v</sup> is the vapor pressure at ambient temperature and ambient RH value.

Furthermore, the diffusion term could be formulated by following equations [97, 98].

$$J_{H_2O,diff} = \frac{\rho \cdot K \cdot K_{rl}}{\mu} \nabla p_c$$
(15)

$$p_{c} = \frac{\sigma \cdot \cos(\theta)}{\left(\frac{K}{\epsilon}\right)^{0.5}} J(s) = \frac{\sigma \cdot \cos(\theta)}{\left(\frac{K}{\epsilon}\right)^{0.5}} \cdot (1.417s - 2.12s^{2} + 1.263s^{3})$$
  
for  $\theta > 90^{\circ}$  (16)

$$K = \frac{\varepsilon^3 \cdot d_f^2}{16 \cdot K_k \cdot (1 - \varepsilon)^2}$$
(17)

$$J_{H_2O,diff} = \frac{\rho \cdot K \cdot K_{rl}}{\mu} \nabla p_c = \frac{\rho \cdot K \cdot K_{rl}}{\mu} \left(\frac{dp_c}{ds}\right) \left(\frac{ds}{dx}\right)$$
$$= \frac{\sigma \cdot \cos(\theta)}{\gamma} \frac{\varepsilon^2 d_f}{4(1-\varepsilon)\sqrt{K_k}} \cdot s^3 (1.417 - 4.24s + 3.789s^2) \frac{ds}{dx}$$
(18)

 $\rho$  is a density of liquid water (kg/m<sup>3</sup>), K is a permeability (m<sup>2</sup>), and K<sub>rl</sub> is a relative permeability.  $\mu$  is a viscosity (m<sup>2</sup>/s) and p<sub>c</sub> is a capillary pressure (Pa).  $\epsilon$  is a porosity value, d<sub>f</sub> is a diameter of fiber (m), and K<sub>k</sub> is a kozeny constant.

Finally, liquid water saturation (s) distribution could be calculated in the porous media along the x-direction in the modeling domain with the following equation [99]. Values of variables for this numerical study are shown in Table 4.3.

$$\left[\frac{\sigma \cdot \cos(\theta)}{\gamma} \frac{\varepsilon^2 d_f}{4(1-\varepsilon)\sqrt{K_k}} \cdot s^3 (1.417 - 4.24s + 3.789s^2) \frac{ds}{dx}\right] + \left[K_{evap} \cdot \frac{1}{A_p} \cdot s \cdot \frac{M_{H_2O}}{RT} \cdot \left\{ \left(p^0 \cdot e^{\left(\frac{-E_a}{k_B \cdot T}\right)}\right) - P^v \right\} \right] = \frac{j}{2F} M^{H_2O}$$
(19)

The results are shown in Fig. 4.6. The liquid water saturation distribution could be compared in the porous media between two open cathode fuel cells

Parameter	Value
Current density (A/m <sup>2</sup> )	3200
GDL contact angle (degree)	140 [100]
MPL porosity	0.5 [100]
GDBL porosity	0.9 [100]
Metal foam porosity	0.94
Fiber diameter of GDBL (m)	9×10 <sup>-6</sup> [101]
Fiber diameter of MPL (m)	1×10 <sup>-6</sup> [98]
Structure diameter of metal foam (m)	78×10 <sup>-6</sup>
Kozeny constant	6 [98]
Kinematic viscosity (m <sup>2</sup> /s)	6.591×10 <sup>-7</sup>
Temperature (K)	313.15
Activation energy of evaporation (eV)	0.449 [95]
Boltzmann constant (eV/K)	8.617×10 <sup>-5</sup> [95]
Pre-exponential factor (Pa)	1.196×10 <sup>11</sup> [95]
Thickness of GDL (MPL/GDBL) (μm)	350 (50/300)
Thickness of metal foam (µm)	1000

 Table 4.3 Values of variables for numerical study [92]

without metal foam and with metal foam. Fig. 4.6 (a) shows the liquid water saturation profile across the MPL and GDBL of the open cathode fuel cell, and Fig. 4.6 (b) shows the liquid water saturation profile across the MPL, GDBL, and metal foam. The open cathode fuel cell with metal foam has higher liquid water saturation in the CCL rather than that without metal foam. Liquid water saturation in the CCL of the fuel cell with metal foam is about 0.76, while the liquid water saturation in the CCL of the fuel cell without metal foam is about 0.42. Based on these data, it could be verified that metal foam flow field in the open cathode fuel cell prevents membrane dehydration and performance drop. However, the open cathode fuel cell with metal foam would have higher concentration losses, if these numerical analysis results were just observed. This is because the open cathode fuel cell with metal foam has higher liquid water saturation value in the CCL. In real experiments, however, the open cathode fuel cell with metal foam has not only smaller ohmic losses, but also concentration losses in the above EIS test results. The different result trend between the numerical analysis and experiment was due to the different dimension. Only one dimension along the x-axis was considered in the modeling domain, while all three-dimensions were considered in the experiments. Thus, metal foam flow field could make more space for air diffusion behind the ribs of cathode current collector which leads to lower concentration losses. In addition, metal foam flow field could not only prevent MEA dehydration, but also have larger contact area which leads to lower ohmic losses. These are why overall performance of the open cathode fuel cell with metal foam could enhance.



Fig. 4.6 Liquid water saturation profile; (a) across the MPL (50 μm) and GDBL (300 μm) (b) across the MPL (50 μm), GDBL (300 μm), and metal foam (1000 μm) [92]

#### **4.3.3** Application to the fuel cell stack

### 4.3.3.1 Polarization curve and power curve

The open cathode fuel cell stack was designed and manufactured to apply the porous metal foam into the fuel cell stack in the cathode side. Fig. 4.7 shows the schematic picture of the open cathode fuel cell stack with metal foam flow field in the cathode side. It has five cells. The serpentine flow field, which was mentioned in Table 4.1, was used in the anode side. Experiments were conducted to prove that using the porous metal foam in the cathode side works not only in the planar unit fuel cell, but also in the fuel cell stack. The experimental results are shown in Fig. 4.8. The maximum power was about 66.2 W, and it is quite a high performance with 5 cells and active area of 25 cm<sup>2</sup>. The maximum power density was about 0.529 W/cm<sup>2</sup>. It shows similar maximum power density with the open cathode planar unit fuel cell with metal foam. Thus, the porous metal foam could be applied to the air-cooled open cathode fuel cell.



Fig. 4.7 A schematic picture of the open cathode fuel cell stack with metal foam flow field [92]



Fig. 4.8 Performance of the open cathode fuel cell stack with metal foam; (a) polarization curve (b) power curve [92]

### 4.4 Summary

In this study, a novel way was introduced to solve the conventional problems such as excessive water evaporation from the membrane, poor transportation of air, and cooling issue of the open cathode PEMFC.

The porous metal foam was inserted into the cathode side of the open cathode planar unit fuel cell. In case of the 52% open area current collector, the maximum power density of the open cathode fuel cell with metal foam increased by 25.1% compared with the conventional open cathode fuel cell without metal foam.

Furthermore, it could be proved that ohmic losses and concentration losses of the open cathode fuel cell with metal foam are smaller than those of the conventional open cathode fuel cell without metal foam by electrochemical impedance spectroscopy test. There are largely because the open cathode fuel cell could have large contact area and large open area for air diffusion with the porous metal foam.

In addition, the open cathode fuel cell with the metal foam could prevent excessive liquid water evaporation and membrane drying out phenomena. It was verified with numerical approach of liquid water saturation profile.

Finally, the porous metal foam was applied into the open cathode fuel cell stack. It was proved that using porous metal foam could enhance the

performance of the air-cooled open cathode fuel cell not only in the planar unit cell, but also in the fuel cell stack.

## **Chapter 5. Concluding remarks**

Performance and efficiency enhancement of the fuel cell systems are highly significant in order to apply fuel cell technology into practice. It is important to increase power per volume of the fuel cell stack, thus fuel cell system could have higher power with smaller size of the fuel cell stack. Therefore, performance analysis of the fuel cell is very important. There are several ways in order to increase the performance of the fuel cell stack. Among them, re-designing of the flow fields is one of the effective method to improve the performance of the fuel cell. There are several types of flow fields in the fuel cell such as parallel flow field, serpentine flow field, porous flow field, and other 3D structures. Thus, many researches about flow fields of the fuel cell had been performed for many years.

This study also examined the flow field of the fuel cell. In this research, the porous flow field of the fuel cell was mainly covered, and performance of the PEMFC with porous flow field was investigated.

In chapter 2, performance change under various severe operating conditions for the PEMFC with porous flow field was studied. It is very important to analyze the performance of the fuel cell under not only normal operating conditions, but also harsh operating conditions. This is because the fuel cell stack should be exposed to various circumstances by users and operated under various different conditions. Even though the performance of the fuel cell with porous flow fields under normal operating conditions were investigated by several researchers, the study on the performance change for the fuel cell with the porous flow field under harsh operating conditions does not exist.

Therefore, porous metal foams were used as the flow distributor in the cathode side of the fuel cell, and performance degradation of the fuel cell under accelerated stress tests was investigated. Two different accelerated stress tests were designed in order to examine the mechanical degradation and electrochemical degradation of the fuel cell with the metal foam. In addition, the performance degradation of the conventional fuel cell with serpentine flow field was also investigated to compare the results. As a result, the fuel cell with metal foam had bigger performance degradation rate rather than the fuel cell with serpentine flow field after accelerated stress tests. However, the performance of the fuel cell with metal foam was still higher than that of the fuel cell with serpentine flow field after the accelerated stress tests. In other words, there was no performance overlapping node between two fuel cells with metal foam flow field and serpentine flow field.

Then, the performance changes under harsh operating conditions such as low SR numbers and extremely low RH values for the fuel cells were examined. The fuel cell with metal foam flow field showed higher air utilization rate and better water management in low SR numbers and extremely low RH values, respectively, rather than the fuel cell with serpentine flow field.

In chapter 3, the PEMFC with porosity gradient in the metal foam flow field was investigated. In general, the maximum power density of the fuel cell with the metal foam flow field is higher than that with the serpentine flow field. In this research, a novel way was introduced in order to make the performance of the fuel cell improve even higher rather than using the conventional metal foam flow field with uniform porosity gradient.

It is significant to have locally non-uniform design of the flow field in the fuel cell since gas, water, temperature, and current density distributions are not uniform in the flow path. Thus, non-uniform porous flow field with porosity gradient was designed. The performance of the fuel cell with porosity gradient in the metal foam enhanced compared with conventional metal foam without porosity gradient. The effects of several porosity gradients and porosity gradient directions on the performance of the fuel cell were studied. Finally, the performance analysis was conducted in the system net power aspect, and the reasons of performance improvement with proper porosity gradient in the metal foam flow field were investigated.

In chapter 4, the performance analysis of air-cooled open cathode PEMFC

with metal foam flow field was performed. Even though air-cooled open cathode PEMFC has lots of merits and high potential to substitute other secondary batteries in the future, it still has several problems needed to be solved. Among them, performance improvement of the air-cooled open cathode PEMFC is essential since performance of the conventional air-cooled open cathode PEMFC is relatively low.

In this research, as inserting the metal foam flow field in the cathode side of the open cathode PEMFC, the conventional problems such as poor mass transport and MEA drying out phenomena could be solved. Finally, the performance of the air-cooled open cathode planar unit cell with metal foam could improve compared with the conventional open cathode PEMFC without the metal foam. Thus, the other application of using metal foam for performance improvement could be found in the fuel cell field.

The reasons of the performance enhancement of the open cathode PEMFC with metal foam were interpreted by numerical analysis. Lastly, the air-cooled open cathode PEMFC stack with metal foam flow field was newly designed and manufactured. Then, it was proved that using metal foam flow field in the cathode side for the fuel cell worked properly not only in the air-cooled open cathode planar unit cell but also air-cooled open cathode fuel cell stack.

In conclusion, performance analysis was performed for the PEMFC with

the metal foam flow field in this study. The performance degradation and response under harsh operating conditions were researched, and the novel way was suggested to improve the performance by introducing porosity gradient in the metal foam flow field. Lastly, performance enhancement of the air-cooled open cathode PEMFC with inserting metal foam flow field in the cathode side was shown for the other application of using metal foam flow field for the performance improvement.

# References

- J. C. Ho, E. C. Saw, L. Y. Y. Lu, and J. S. Liu, "Technological barriers and research trends in fuel cell technologies: A citation network analysis," *Technol. Forecast. Soc. Change*, vol. 82, no. 1, pp. 66–79, 2014.
- [2] F. Jing, M. Hou, W. Shi, J. Fu, H. Yu, P. Ming, and B. Yi, "The effect of ambient contamination on PEMFC performance," *J. Power Sources*, vol. 166, no. 1, pp. 172–176, 2007.
- [3] S. G. Kandlikar and Z. Lu, "Thermal management issues in a PEMFC stack A brief review of current status," *Appl. Therm. Eng.*, vol. 29, no. 7, pp. 1276–1280, 2009.
- [4] E. Springer, A. Zawodzinski, M. S. Wilson, and S. Golfesfeld,
   "Characterization of polymer electrolyte fuel cells using AC impedance spectroscopy," *Journal of The Electrochemical Society*, 1996.
- [5] R. O'Hayre, S. W. Cha, W. Colella, and F. B. Prinz, *Fuel cell fundamentals*. 2016.
- [6] S. Shimpalee, S. Greenway, and J. W. Van Zee, "The impact of channel path length on PEMFC flow-field design," *J. Power Sources*, vol. 160, no. 1, pp. 398–406, 2006.

- [7] Y. Wang, L. Yue, and S. Wang, "New design of a cathode flow-field with a sub-channel to improve the polymer electrolyte membrane fuel cell performance," *J. Power Sources*, vol. 344, pp. 32–38, 2017.
- [8] A. Su, Y. C. Chiu, and F. B. Weng, "The impact of flow field pattern on concentration and performance in PEMFC," *Int. J. Energy Res.*, vol. 29, no. 5, pp. 409–425, 2005.
- [9] I. M. Kong, A. Jung, Y. S. Kim, and M. S. Kim, "Numerical investigation on double gas diffusion backing layer functionalized on water removal in a proton exchange membrane fuel cell," *Energy*, vol. 120, pp. 478–487, 2017.
- [10] K. D. Baik and I. S. Seo, "Metallic bipolar plate with a multi-hole structure in the rib regions for polymer electrolyte membrane fuel cells," *Appl. Energy*, vol. 212, no. July 2017, pp. 333–339, 2018.
- [11] Y. Cai, Z. Fang, B. Chen, T. Yang, and Z. Tu, "Numerical study on a novel 3D cathode flow field and evaluation criteria for the PEM fuel cell design," *Energy*, vol. 161, pp. 28–37, 2018.
- [12] Y. Yin, X. Wang, X. Shangguan, J. Zhang, and Y. Qin, "Numerical investigation on the characteristics of mass transport and performance of PEMFC with baffle plates installed in the flow channel," *Int. J. Hydrogen Energy*, vol. 43, no. 16, pp. 8048–8062, 2018.

- [13] Z. Niu, L. Fan, Z. Bao, and K. Jiao, "Numerical investigation of innovative 3D cathode flow channel in proton exchange membrane fuel cell," *Int. J. Energy Res.*, vol. 42, no. 10, pp. 3328–3338, 2018.
- [14] C. J. Tseng, B. T. Tsai, Z. S. Liu, T. C. Cheng, W. C. Chang, and S. K.
   Lo, "A PEM fuel cell with metal foam as flow distributor," *Energy Convers. Manag.*, vol. 62, pp. 14–21, 2012.
- [15] D. K. Shin, J. H. Yoo, D. G. Kang, and M. S. Kim, "Effect of cell size in metal foam inserted to the air channel of polymer electrolyte membrane fuel cell for high performance," *Renew. Energy*, vol. 115, pp. 663–675, 2018.
- B. T. Tsai. C. J. Tseng, Z. S. Liu., C. H. Wang, C. I. Lee, C. C. Yang, and S. K. Lo, "Effects of flow field design on the performance of a PEM fuel cell with metal foam as the flow distributor," *Int. J. Hydrogen Energy*, vol. 37, no. 17, pp. 13060–13066, 2012.
- [17] F. Ting, C. Hsieh, W. Weng, and J. Lin, "Effect of operational parameters on the performance of PEMFC assembled with Au-coated Ni-foam," *Int. J. Hydrogen Energy*, vol. 37, no. 18, pp. 13696–13703, 2012.
- [18] A. Kumar and R. G. Reddy, "Modeling of polymer electrolyte membrane fuel cell with metal foam in the flow-field of the

bipolar/end plates," J. Power Sources, vol. 114, no. 1, pp. 54–62, 2003.

- [19] A. Jo, S. Ahn, K. Oh, W. Kim, and H. Ju, "Effects of metal foam properties on flow and water distribution in polymer electrolyte fuel cells (PEFCs)," *Int. J. Hydrogen Energy*, vol. 43, no. 30, pp. 14034– 14046, 2018.
- [20] A. Jo and H. Ju, "Numerical study on applicability of metal foam as flow distributor in polymer electrolyte fuel cells (PEFCs)," *Int. J. Hydrogen Energy*, vol. 43, no. 30, pp. 14012–14026, 2018.
- [21] M. Saeedan, "Numerical thermal analysis of nanofluid flow through the cooling channels of a polymer electrolyte membrane fuel cell filled with metal foam," *International Journal of Energy Research*, no. September 2019, pp. 1–19, 2020.
- [22] C. Tseng, Y. Heush, C. Chiang, Y. Lee, and K. Lee, "Application of metal foams to high temperature PEM fuel cells," *Int. J. Hydrogen Energy*, vol. 41, no. 36, pp. 16196–16204, 2016.
- [23] S. Li and B. Sund, "Three-dimensional modeling and investigation of high temperature proton exchange membrane fuel cells with metal foams as flow distributor," *Int. J. Hydrogen Energy*, vol. 2, 2017.
- [24] M. Hampe and T. Reiber, "Investigation of porous metal-based 3D-

printed anode GDLs for tubular high temperature proton exchange membrane fuel cells," *materials*, pp. 1–12, 2020.

- [25] E. Afshari, M. Ziaei-rad, and Z. Shariati, "A study on using metal foam as coolant fluid distributor in the polymer electrolyte membrane fuel cell," *Int. J. Hydrogen Energy*, vol. 41, no. 3, pp. 1902–1912, 2015.
- Y. Wu, J. I. S. Cho, M. Whiteley, L. Rasha, T.P. Neville, R. Ziesche,
  R. Xu, R. Owen, N. Kulkarni, J. Hack, M. Maier, N. Kardjilov, H.
  Markotter, I. Manke, F.R. Wang, P. R. Shearing, and D. J. L. Brett,
  "Characterization of water management in metal foam flow-field
  based polymer electrolyte fuel cells using in-operando neutron
  radiography," *Int. J. Hydrogen Energy*, vol. 5, 2019.
- [27] L. Weng and C. Tseng, "Effects of assembling method and force on the performance of proton-exchange membrane fuel cells with metal foam flow field," *International Journal of Energy Research*, no. May, pp. 1–7, 2020.
- [28] E. Afshari, "Computational analysis of heat transfer in a PEM fuel cell with metal foam as a flow field," *J. Therm. Anal. Calorim.*, vol. 139, no. 4, pp. 2423–2434, 2020.
- [29] R. Liu, W. Zhou, S. Li, F. Li, and W. Ling, "Performance

improvement of proton exchange membrane fuel cells with compressed nickel foam as flow field structure," *Int. J. Hydrogen Energy*, vol. 45, no. 35, pp. 17833–17843, 2020.

- [30] Y. Nagahara, S. Sugawara, and K. Shinohara, "The impact of air contaminants on PEMFC performance and durability," *J. Power Sources*, vol. 182, pp. 422–428, 2008.
- [31] J. Yu, E. S. Lett, J. Yu, T. Matsuura, Y. Yoshikawa, and N. Islam, "In situ analysis of performance degradation of a PEMFC under nonsaturated humidification," *Electrochemical and Solid-State Letters*, vol. 8, no. 3, pp. A156–A158, 2005.
- [32] Z. Wang, P. Zuo, Y. Chu, Y. Shao, and G. Yin, "Durability studies on performance degradation of Pt / C catalysts of proton exchange membrane fuel cell," *Int. J. Hydrogen Energy*, vol. 34, no. 10, pp. 4387–4394, 2009.
- [33] P. Yu, M. Pemberton, and P. Plasse, "PtCo / C cathode catalyst for improved durability in PEMFCs," *J. Power Sources*, vol. 144, no. November 2004, pp. 11–20, 2005.
- [34] Y. Y. Jo, E. A. Cho, J. H. Kim, T. H. Lim, I. H. Oh, J. H. Jang, and H. J. Kim, "Effects of a hydrogen and air supply procedure on the performance degradation of PEMFCs," *Int. J. Hydrogen Energy*, vol.

35, no. 23, pp. 13118–13124, 2010.

- [35] J. H. Kim, E. A. Cho, J. H. Jang, H. J. Kim, T. H. Lim, I. H. Oh, J. J. Ko, and S. C. Oh, "Effects of cathode inlet relative humidity on PEMFC durability during startup shutdown cycling : I .
  Electrochemical Study," *Journal of The Electrochemical Society*, vol. 157, no. 1, pp. B104-B112, 2010.
- [36] Z. Qi, H. Tang, Q. Guo, and B. Du, "Investigation on ' saw-tooth ' behavior of PEM fuel cell performance during shutdown and restart cycles," *J. Power Sources*, vol. 161, pp. 864–871, 2006.
- [37] A. Kannan, A. Kabza, and J. Scholta, "Long term testing of start e stop cycles on high temperature PEM fuel cell stack," *J. Power Sources*, vol. 277, pp. 312–316, 2015.
- [38] J. Kang and J. Kim, "Membrane electrode assembly degradation by dry / wet gas on a PEM fuel cell," *Int. J. Hydrogen Energy*, vol. 35, no. 23, pp. 13125–13130, 2010.
- [39] B. Wu, M. Zhao, W. Shi, and W. Liu, "The degradation study of Nafion / PTFE composite membrane in PEM fuel cell under accelerated stress tests," *Int. J. Hydrogen Energy*, vol. 39, no. 26, pp. 14381–14390, 2014.
- [40] R. Sharma and S. M. Andersen, "An opinion on catalyst degradation

mechanisms during catalyst support focused accelerated stress test (AST) for proton exchange membrane fuel," *Appl. Catal. B Environ.*, vol. 239, no. August, pp. 636–643, 2018.

- [41] D. Schonvogel, M. Rastedt, P. Wagner, M. Wark, and A. Dyck,
  "Impact of accelerated stress tests on high temperature PEMFC degradation," *Fuel Cells*, no. 4, pp. 480–489, 2016.
- [42] R. Petrone and D. Hissel, "Accelerated stress test procedures for PEM fuel cells under actual load constraints : State-of-art and proposals," *Int. J. Hydrogen Energy*, vol. 0, 2015.
- [43] J. Park, J. E. Soc, J. Park, L. Wang, S. G. Advani, and A. K. Prasad,
  "Durability analysis of nafion / hydrophilic pretreated PTFE membranes for PEMFCs," *Journal of The Electrochemical Society*, vol 159, no. 12, pp. F864-F870, 2012.
- [44] J. Han, J. Han, and S. Yu, "Experimental analysis of performance degradation of 3-cell PEMFC stack under dynamic load cycle," *Int. J. Hydrogen Energy*, vol. 45, no. 23, pp. 13045–13054, 2020.
- [45] Z. Zheng, F. Yang, C. Lin, F. Zhu, S. Shen, G. Wei, and J. Zhang,
  "Design of gradient cathode catalyst layer (CCL) structure for mitigating Pt degradation in proton exchange membrane fuel cells (PEMFCs) using mathematical method," *J. Power Sources*, vol. 451,

no. January, pp. 227729, 2020.

- [46] Z. Liu, J. Chen, H. Liu, C. Yan, Y. Hou, and Q. He, "Anode purge management for hydrogen utilization and stack durability improvement of PEM fuel cell systems," *Appl. Energy*, vol. 275, no. December 2019, pp. 115110, 2020.
- [47] T. Morawietz, K. A. Friedrich, P. G. Rocha, R. Hiesgen, and P.
   Gazdzicki, "Local impact of load cycling on degradation in polymer electrolyte fuel cells," *Appl. Energy*, vol. 259, no. May 2019, pp. 114210, 2020.
- [48] N. Bussayajarn, H. Ming, K. K. Hoong, W. Y. Ming Stephen, and C.
  S. Hwa, "Planar air breathing PEMFC with self-humidifying MEA and open cathode geometry design for portable applications," *Int. J. Hydrogen Energy*, vol. 34, no. 18, pp. 7761–7767, 2009.
- [49] U. H. Jung, S. U. Jeong, K. T. Park, H. M. Lee, K. Chun, D. W. Choi, and S. H. Kim, "Improvement of water management in air-breathing and air-blowing PEMFC at low temperature using hydrophilic silica nano-particles," *Int. J. Hydrogen Energy*, vol. 32, no. 17, pp. 4459– 4465, 2007.
- [50] T. Fabian. J. D. Posner, R. O'Hayre, S. W. Cha, J. K. Eaton, F. B.Prinz, and J. G. Santiago, "The role of ambient conditions on the

performance of a planar, air-breathing hydrogen PEM fuel cell," J. *Power Sources*, vol. 161, no. 1, pp. 168–182, 2006.

- [51] R. W. Atkinson, J. A. Rodgers, M. W. Hazard, R. O. Stroman, and B.
  D. Gould, "Influence of cathode gas diffusion media porosity on opencathode fuel cells," *J. Electrochem. Soc.*, vol. 165, no. 11, pp. F1002– F1011, 2018.
- [52] W. Ying, J. Ke, W. Y. Lee, T. H. Yang, and C. S. Kim, "Effects of cathode channel configurations on the performance of an air-breathing PEMFC," *Int. J. Hydrogen Energy*, vol. 30, no. 12, pp. 1351–1361, 2005.
- [53] Y. Tabe, S. K. Park, K. Kikuta, T. Chikahisa, and Y. Hishinuma,
  "Effect of cathode separator structure on performance characteristics of free-breathing PEMFCs," *J. Power Sources*, vol. 162, no. 1, pp. 58– 65, 2006.
- [54] J. Zhao, Q. Jian, and Z. Huang, "Experimental and theoretical study on improving the operating characteristics of an open-cathode PEMFC stack by generating periodic disturbances at anode," *Energy Convers. Manag.*, vol. 196, no. June, pp. 1433–1444, 2019.
- [55] S. Strahl, N. Gasamans, J. Llorca, and A. Husar, "Experimental analysis of a degraded open-cathode PEM fuel cell stack," *Int. J.*

Hydrogen Energy, vol. 39, no. 10, pp. 5378–5387, 2014.

- [56] R. A. Silva, T. Hashimoto, G. E. Thompson, and C. M. Rangel,
  "Characterization of MEA degradation for an open air cathode PEM fuel cell," *Int. J. Hydrogen Energy*, vol. 37, no. 8, pp. 7299–7308, 2012.
- [57] K. Ou, W. W. Yuan, M. Choi, S. Yang, and Y. B. Kim, "Performance increase for an open-cathode PEM fuel cell with humidity and temperature control," *Int. J. Hydrogen Energy*, vol. 42, no. 50, pp. 29852–29862, 2017.
- [58] D. T. Santa Rosa, D. G. Pinto, V. S. Silva, R. A. Silva, and C. M. Rangel, "High performance PEMFC stack with open-cathode at ambient pressure and temperature conditions," *Int. J. Hydrogen Energy*, vol. 32, no. 17, pp. 4350–4357, 2007.
- [59] A. M. López-Sabirón, J. Barroso, V. Roda, J. Barranco, A. Lozano, and F. Barreras, "Design and development of the cooling system of a 2 kW nominal power open-cathode polymer electrolyte fuel cell stack," *Int. J. Hydrogen Energy*, vol. 37, no. 8, pp. 7289–7298, 2012.
- [60] A. Schmitz, M. Tranitz, S. Eccarius, A. Weil, and C. Hebling,"Influence of cathode opening size and wetting properties of diffusion layers on the performance of air-breathing PEMFCs," *J. Power*

Sources, vol. 154, no. 2, pp. 437-447, 2006.

- [61] C. Zhao, S. Xing, W. Liu, and H. Wang, "Comprehensive anode parameter study for an open-cathode PEMFC," *energy & fuels*, vol. 34, pp. 7582-7590, 2020.
- [62] C. Zhao, S. Xing, M. Chen, W. Liu, and H. Wang, "Optimal design of cathode flow channel for air-cooled PEMFC with open cathode," *Int. J. Hydrogen Energy*, vol. 45, no. 35, pp. 17771–17781, 2020.
- [63] K. D. Baik and S. H. Yang, "Improving open-cathode polymer electrolyte membrane fuel cell performance using multi-hole separators," *Int. J. Hydrogen Energy*, vol. 45, no. 15, pp. 9004–9009, 2020.
- [64] L. Vichard, R. Petrone, F. Harel, A. Ravey, P. Venet, and D. Hissel,
  "Long term durability test of open-cathode fuel cell system under actual operating conditions," *Energy Convers. Manag.*, vol. 212, no. January, pp. 112813, 2020.
- [65] W. Yuan, Y. Tang, M. Pan, Z. Li, and B. Tang, "Model prediction of effects of operating parameters on proton exchange membrane fuel cell performance," *Renew. Energy*, vol. 35, no. 3, pp. 656–666, 2010.
- [66] M. Amirinejad, S. Rowshanzamir, and M. H. Eikani, "Effects of operating parameters on performance of a proton exchange membrane

fuel cell," vol. 161, pp. 872-875, 2006.

- [67] H. Lee, T. Kim, W. Sim, S. Kim, B. Ahn, T. Lim, and K. park,
  "Pinhole formation in PEMFC membrane after electrochemical degradation and wet / dry cycling test," *Korean J. Chem. Eng*, vol. 28, no. 2, pp. 487–491, 2011.
- [68] F. A. De Bruijn, V. A. T. Dam, and G. J. M. Janssen, "Review : durability and degradation issues of PEM fuel cell components," *Fuel Cells*, no. 1, pp. 3–22, 2008.
- [69] J. Zhao, S. Shahgaldi, X. Li, and Z. S. Liu, "Experimental observations of microstructure changes in the catalyst layers of proton exchange membrane fuel cells under wet-dry cycles," *Journal of The Electrochemical Society*, vol. 165, no. 6, pp. 3337–3345, 2018.
- [70] Q. Yan, H. Toghiani, and H. Causey, "Steady state and dynamic performance of proton exchange membrane fuel cells (PEMFCs) under various operating conditions and load changes," *J. Power Sources*, vol. 161, no. 1, pp. 492–502, 2006.
- [71] L. Wang, A. Husar, T. Zhou, and H. Liu, "A parametric study of PEM fuel cell performances," vol. 28, pp. 1263–1272, 2003.
- [72] J. Zhang, Y. Tang, C. Song, Z. Xia, H. Li, H. Wang, and J. Zhang,"PEM fuel cell relative humidity (RH) and its effect on performance at
high temperatures," *Electrochim. Acta*, vol. 53, no. 16, pp. 5315–5321, 2008.

- [73] K. C. Neyerlin, H. A. Gasteiger, C. K. Mittelsteadt, J. Jorne, and W.
   Gu, "Effect of relative humidity on oxygen reduction kinetics in a
   PEMFC," *J. Electrochem. Soc.*, vol. 152, no. 6, pp. A1073, 2005.
- [74] P. Lettenmeier, S. Kolb, N. Sata, A. Fallisch, L. Zielke, S. Thiele, A.
  S. Gago, and K. A. Friedrich, "Comprehensive investigation of novel pore-graded gas diffusion layers for high-performance and cost-effective proton exchange membrane electrolyzers," *Energy Environ*. *Sci.*, vol. 10, no. 12, pp. 2521–2533, 2017.
- [75] T. A. Aarhaug and A. M. Svensson, "Degradation rates of PEM fuel cells running at open circuit voltage," *The Electrochemical Society*, vol. 3, no. 1, pp. 775–780, 2006.
- [76] W. Liu and D. Zuckerbrod, "In situ detection of hydrogen peroxide in PEM fuel cells," *J. Electrochem. Soc*, pp. 1165–1170, 2005.
- [77] X. Huang, R. Solasi, Y. Zou, M. Feshler, K. Reifsnider, D. Condit, S. Burlatsky, and T. Madden, "Mechanical endurance of polymer electrolyte membrane and PEM fuel cell durability," *Wiley InterScience*, pp. 2346–2357, 2006.
- [78] G. Scherer, "Study of radiation-grafted FEP-g-polystyrene membranes

as polymer electrolytes in fuel cells," vol. 40, no. 3, pp. 345–353, 1995.

- [79] Z. Bao, Z. Niu, and K. Jiao, "Numerical simulation for metal foam two-phase flow field of proton exchange membrane fuel cell," *Int. J. Hydrogen Energy*, vol. 44, no. 12, pp. 6229–6244, 2019.
- [80] E. Afshari and N. Baharlou Houreh, "Performance analysis of a membrane humidifier containing porous metal foam as flow distributor in a PEM fuel cell system," *Energy Convers. Manag.*, vol. 88, pp. 612–621, 2014.
- [81] S. Shimpalee, S. Greenway, D. Spuckler, and J. W. Van Zee,
  "Predicting water and current distributions in a commercial-size
  PEMFC," *J. Power Sources*, vol. 135, no. 1–2, pp. 79–87, 2004.
- [82] S. Um, C.-Y. Wang, and K. S. Chen, "Computational fluid dynamics modeling of proton exchange membrane fuel cells," *J. Electrochem. Soc.*, vol. 147, no. 12, pp. 4485–4493, 2000.
- [83] D. G. Kang, D. K. Lee, J. M. Choi, D. K. Shin, and M. S. Kim, "Study on the metal foam flow field with porosity gradient in the polymer electrolyte membrane fuel cell," *Renewable Energy*, vol. 156, pp. 931-941, 2020.
- [84] P. M. Adler, C. G. Jacquin, and J. A. Quiblier, "Flow in simulated

porous media," Int. J. Multiph. Flow, vol. 16, no. 4, pp. 691–712, 1990.

- [85] A. Koponen, M. Kataja, and J. Timonen, "Permeability and effective porosity of porous media," *Phys. Rev. E - Stat. Physics, Plasmas, Fluids, Relat. Interdiscip. Top.*, vol. 56, no. 3, pp. 3319–3325, 1997.
- [86] J. Larminie and A. Dicks, Fuel cell systems explained, vol. 93. 2001.
- [87] M. Kim, C. Kim, and Y. Sohn, "Application of metal foam as a flow field for PEM fuel cell stack," *Fuel Cells*, vol. 18, no. 2, pp. 123–128, 2018.
- [88] R. G. Holdich, Fundamentals of particle technology, 2002.
- [89] J. P. Bonnet, F. Topin, and L. Tadrist, "Flow laws in metal foams : compressibility and pore size effects," pp. 233–254, 2008.
- [90] B. F. Topin, J. Bonnet, B. Madani, and L. Tadrist, "Experimental analysis of multiphase flow in metallic foam : flow laws , heat transfer and convective boiling ," *Advanced Engineering Materials*, no. 9, pp. 890–899, 2006.
- [91] M. R. S. Shirazy and L. G. Fréchette, "International journal of heat and mass transfer capillary and wetting properties of copper metal foams in the presence of evaporation and sintered walls," *Int. J. Heat Mass Transf.*, vol. 58, no. 1–2, pp. 282–291, 2013.

- [92] D. G, Kang, C. Park, I. S. Lim, S. H. Choi, D. K. Lee, and M. S. Kim, "Performance enhancement of air-cooled open cathode polymer electrolyte membrane fuel cell with inserting metal foam in the cathode side," *Int. J. Hydrogen Energy*, vol. 45, pp. 27622-27631, 2020.
- [93] S. U. Jeong, E. A. Cho, H. J. Kim, T. H. Lim, I. H. Oh, and S. H. Kim, "Effects of cathode open area and relative humidity on the performance of air-breathing polymer electrolyte membrane fuel cells," *J. Power Sources*, vol. 158, no. 1, pp. 348–353, 2006.
- [94] W. Shi, E. Kurihara, and N. Oshima, "Effect of capillary pressure on liquid water removal in the cathode gas diffusion layer of a polymer electrolyte fuel cell," *J. Power Sources*, vol. 182, no. 1, pp. 112–118, 2008.
- [95] S. Strahl, A. Husar, and A. A. Franco, "Electrode structure effects on the performance of open-cathode proton exchange membrane fuel cells: A multiscale modeling approach," *Int. J. Hydrogen Energy*, vol. 39, no. 18, pp. 9752–9767, 2014.
- [96] M. Eikerling, "Water management in cathode catalyst layers of PEM fuel cells," J. Electrochem. Soc., vol. 153, no. 3, pp. 58–70, 2006.
- [97] Z. Zhan, J. Xiao, D. Li, M. Pan, and R. Yuan, "Effects of porosity

distribution variation on the liquid water flux through gas diffusion layers of PEM fuel cells," *J. Power Sources*, vol. 160, no. 2 SPEC. ISS., pp. 1041–1048, 2006.

- [98] Z. Zhan, J. Xiao, Y. Zhang, M. Pan, and R. Yuan, "Gas diffusion through differently structured gas diffusion layers of PEM fuel cells," *Int. J. Hydrogen Energy*, vol. 32, no. 17, pp. 4443–4451, 2007.
- [99] S. Strahl, A. Husar, P. Puleston, and J. Riera, "Performance improvement by temperature control of an open-cathode PEM fuel cell system," *Fuel Cells*, vol. 14, no. 3, pp. 466–478, 2014.
- [100] I. M. Kong, A. Jung, and M. S. Kim, "Investigations on the double gas diffusion backing layer for performance improvement of self-humidified proton exchange membrane fuel cells," *Appl. Energy*, vol. 176, pp. 149–156, 2016.
- [101] A. Tamayol, F. McGregor, and M. Bahrami, "Single phase throughplane permeability of carbon paper gas diffusion layers," *J. Power Sources*, vol. 204, pp. 94–99, 2012.

## 국문초록

고분자 전해질막 연료전지 시스템은 산소와 수소의 전기화학반응 을 이용하여 전기를 발전시키는 시스템이다. 연료전지는 부산물로 순수한 물만을 배출하기 때문에 수년간 친환경 대체 에너지 기술로 각광받고 있다. 그러나 연료전지 기술 상용화를 위해서는 아직 해결 해야할 몇 가지 난제들이 남아있다. 그 중에서 연료전지 시스템의 출력 및 효율을 높이는 것은 매우 중요하다. 연료전지 시스템의 성 능을 높이기 위해서는, 전기화학반응 손실들을 최소화해야 하는데, 전기화학 손실을 줄이는 방법으로 연료전지 유로를 새롭게 설계하 는 방법이 있다. 따라서, 많은 연구자들이 연료전지 유로 설계 관하 여 연구를 수행하였고 현재까지 평행 구조 유로, 사형 구조 유로, 다공성 유로, 다른 3D 구조체 유로 등 여러가지 종류의 연료전지 유로가 발달되어 왔다.

본 연구에서는 다공성 유로를 적용한 고분자 전해질막 연료전지 의 성능에 관하여 연구를 수행하였다. 메탈폼(metal foam) 유로를 연료전지 양극 유로에 적용하였고, 첫째로, 극한 상황에서 메탈폼 유로를 적용한 연료전지의 성능 변화를 연구하였다. 가속 스트레스 시험을 설계하여 다공성 유로를 적용한 연료전지 성능의 기계적 열 화 및 전기화학적 열화 현상을 실험적으로 관찰하였고 사형 구조 유로를 적용한 연료전지 성능 열화 현상 또한 관찰하여 두 실험 결 과를 비교 분석하였다. 또한, 공급 연료가 부족한 경우 혹은 극심하 게 낮은 가습 조건과 같은 극한 상황 조건에서 메탈폼 유로를 적용 한 연료전지와 사형 구조 유로를 적용한 연료전지의 성능 변화를 관찰하였다. 결과적으로, 메탈폼을 적용한 연료전지의 성능 열화 비 율이 사형 구조 유로를 적용한 연료전지의 성능 열화 비 율이 사형 구조 유로를 적용한 연료전지의 성능 영화 비 율이 사형 구조 유로를 적용한 연료전지의 성능 영화 비 율이 사형 구조 유로를 적용한 연료전지의 성능 여료 가 다. 가속 스트레스 시험 이후에 메탈폼을 적용한 연료전지의 성능이 사 형 구조 유료를 적용한 연료전지의 성능보다 여전히 높았다. 그리고 극한 작동 조건에서 다공성 유로를 적용한 연료전지가 높은 연료 이용률과 보다 효과적인 물 관리를 보였다.

다음으로, 본 연구에서는 공극률이 점차적으로 변하는 다공성 유 로를 연료전지 양극 유로에 적용하였다. 연료전지 유로 내에서 전류 밀도, 온도, 공급 기체, 생성된 물의 분포가 일정하지 않기 때문에 이러한 연료전지 특성을 반영한 유로의 국부 설계는 불가피하다. 그 러므로, 공극률이 점차적으로 변하는 다공성 유로를 국부 설계하였 고, 여러 실험을 통하여 다공성 유로의 국부 설계로 인해 그렇지 않 은 일반적인 다공성 유로를 적용하였을 때 보다 연료전지의 성능이 향상됨을 확인할 수 있었다. 공극률이 점차적으로 변하는 다공성 유 로를 연료전지에 적용하였을 때 공극률이 균일한 기존의 다공성 유 로를 적용하였을 때 보다 연료전지의 최대 전력 밀도가 8.23% 증가 하였다. 또한, 연료전지의 성능 향상을 연료전지 시스템 소모 전력 관점에서 분석하였고, 공극률이 점차적으로 변하는 국부 설계된 다 공성 유로를 연료전지에 적용하였을 때 성능이 향상되는 원인을 연 구하였다.

마지막으로, 기존의 양극 개방형 공냉식 연료전지의 문제점을 해 결 하기 위하여 다공성 유로를 설계하여 적용하였고, 연료전지의 성 능을 향상시킬 수 있었다. 전해질막에서 과도한 물 증발 및 공기 공 급 부족과 같은 기존의 양극 개방형 연료전지의 문제점들을 해결하 기 위하여 메탈폼 유로를 양극 개방형 연료전지 단위 셀에 적용하 였다. 실험 연구를 통하여 메탈폼 유로를 양극 개방형 연료전지에 적용하였을 경우 그렇지 않은 경우 보다 최대 전력 밀도가 25.1% 향상됨을 확인하였고, 메탈폼 유로를 적용한 양극 개방형 연료전지 는 작은 저항 손실 및 농도 손실을 보였다. 또한, 메탈폼 유로를 적 용한 양극 개방형 연료전지는 전해질막이 과도하게 마르는 현상을 방지할 수 있다는 것을 수치해석을 통하여 입증하였다. 마지막으로, 메탈폼 유로를 적용 가능한 양극 개방형 공냉식 연료전지 스택 (stack)을 설계 및 제작하였고, 연료전지 스택에서 연료전지 단위 셀과 상응하는 높은 성능을 보이는 것을 확인할 수 있었다.

## 주요어: 고분자 전해질막 연료전지, 다공성 유로, 극한 상황, 공극률 변화, 양극 개방형, 성능 향상

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