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Influence of water transport properties through gas diffusion layer on flooding in PEFC

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How the property of liquid water transport through a gas diffusion layer (GDL) influences the cell performance on electrode flooding was investigated by examining the cell performance and measuring the pressure to dehydrate liquid water from a GDL on a polymer electrolyte fuel cell (PEFC). A PEFC is required to operate under high humidity condition and high gas utilization aimed at high performance and high system efficiency. However, conversely, sudden decrease of the cell performance is caused by the water flooding in some types of GDL which disturbs the gas diffusion to reaction area under above conditions. The GDLs fabricated by four manufacturers which have different characters of structure, affinities for water, with and without through-holes, with and without a water management layer were examined by the single cell generation examination. Focusing attention on the experimental fact of the recent researches, the GDL is impregnated with water when electrode flooding is caused. As the examination outside of the cell that imitates the actual generation, the property of liquid water transport was evaluated by measuring dehydration pressure of through plane direction from water impregnated GDL. By the comparison limiting current determined by the IV curve with dehydration pressure, it was found that strong negative correlation existed between flooding phenomena in the GDL and pressure to dehydrate from the GDL.
Key words: PEFC, water management, flooding, GDL, gas diffusivity

1. INTRODUCTION

Regarding a PEFC, the influence of water transport properties through GDL on flooding in PEFC was investigated. On a PEFC, high humidity operation is required for high performance because it is necessary to contain much water in proton exchange membrane and ionomer at catalyst layer (CL). Additionally, high gas utilization is required for high system efficiency. However, significant decrease of a cell performance is caused by condensed water, which causes the diffusional inhibition of reactant gas on electrodes which consist of GDL and CL, and in gas channels under these conditions. There are two different condensed water problems, which can be considered as different phenomena. One is a diffusional inhibition by accumulated water on electrodes, which is called flooding and the other is by water droplet which plugged gas channel, which is called plugging in general. The behavior of water droplet on plugging was reported by investigating to monitor pressure drop of cell and to observe visualization cell [1-3]. Furthermore, it is elucidating dominant factor which is hydrophilicity of gas channel [4].

On the other hand, compared to plugging, water transport properties through GDL on flooding remain to be elucidated because GDL has complex fabric structure, property and difficulty of direct observation. In recent years, lots of experimental facts and simulation results are obtained [5-11]. However, these current researches still have a variety of preconditions and exceptions. The purpose of this study is to investigate how the property of liquid water transport through a GDL influences the cell performance on electrode flooding by testing many types of GDL and find dominant factor of flooding. The GDLs fabricated by four manufacturers which have different characters of structure, affinities for water, with and without through-holes, with and without a water management layer (WML) were examined by the single cell generation examination. Focusing attention on the experimental fact of the recent researches, the GDL is impregnated with water when electrode flooding is caused [12]. As the examination outside of the cell that imitates the actual generation, the property of liquid water transport was evaluated by measuring dehydration pressure of through plane direction from water impregnated GDL.

By the comparison limiting current determined by the IV curve with dehydration pressure, it was found that strong negative correlation existed between flooding phenomena in the GDL and pressure to dehydrate from the GDL.

2. EXPERIMENTAL

2.1 Preparation of cells for test

Selected GDL: GDL specifications are shown in Table Ⅰ. Gas permeability was measured by experiment which is explained at 2.2. Many types of GDL were used for tests. Some GDLs were added hydrophobicity with PTFE. One GDL was coated by WML.

Hydrophobic treatment and WML coating: The procedures of hydrophobic treatment and WML coating are shown in Table Ⅱ. PTFE dispersion agent was added to GDL to create hydrophobicity. It was dried few minutes and sintered at 350℃ for 15 minutes in the atmosphere. Mean PTFE content of GDLs are shown in Table I. The hydrophobic WML containing Vulcan Black (30nm, 254m^2/g) and PTFE fine powder (200~250nm) were applied to the GDL using dry coating method [13-15]. The PTFE content of WML was 30wt%.

Membrane electrode assembly (MEA) preparation: MEA preparation is shown in Table III. MEA was combined PRIMEA 5510 which is fabricated by Japan Goretex and GDLs which are shown in table I.

Single cell preparation: Cell specifications and configuration are shown in Table III and Fig. 1 respectively. In this study single cell was used to evaluation. Carbon separator which had 16 gas channels by machined was used.

Table I. GDL specifications

Type	Name for legends	Thick -ness	Bulk density	Mean PTFE content
		μm	g/cm^3	wt%
TGPH030	030-0	111	0.38	0
	030-12			12.3
TGPH060	060-0	216	0.40	0
	060-12			16.6
	060-x			N/A*d
TGPH090	090-0	283	0.44	0
	090-12			13.7
	090-12-WML*a			13.7
Type A	A-0	189	0.37	0
	A-12			17.4
	A-30			61.4
Type B*b	B	203	0.38	0
Type C*c	C-0	189	0.38	0
	C-12			14.8
	C-30			50.1
Type D*c	D-0	189	0.37	0
	D-12			21.5
	D-30			65.6
Type E	E-0	300	0.22	0
	E-x			N/A*d
	E-12			13.7
Type F	F-0	121	0.31	0
	F-12			17.1
Type G	G-0	132	0.28	0
	G-12			22.3

*a Amount of WML=2mg/cm^2, thickness of WML=20μm
*b Hydrophilic treatment
*c Diameter of through-hole of Type C and D are 90μm and 184μm respectively, at intervals of 700μm
*d N/A means not available because of treated by manufacturer

Table II. GDL and WML preparations

GDL	Substrate	Carbon paper, felt
	Hydrophobizing agent	PTFE dispersion
	Conc. of dispersion	12wt%, 30wt%
	Heat-treating	350℃ for 15min.
WML	Base material	Vulcan black
	Coating method	Dry
	Hydrophobizing agent	PTFE fine powder
	Carbon : PTFE	7:3
	Heat-treating	2times at 350℃ for 30min.

2.2 Experimental methodology

Observation of figuration: The surface and cross section of GDLs were observed by scanning electron microscope (SEM) paying attention on carbon fibers, binder which bind carbon fibers and structure of GDLs. Furthermore, the surface of carbon fiber of hydrophilicity treated GDL by chemical roughening process was observed by atomic force microscope (AFM).

Table III. Cell specifications

MEA	CCM	Electrolyte mem.	Perfluorosulfonic acid
		Anode cat.	Pt, 0.3mg/cm^2
		Cathode cat.	
	GDL	Refer Table I	
	WML		
Separator		Active area	30mm×150mm
		Material	Carbon
		Gas channel	Straight
		Gas flow direction	Counter

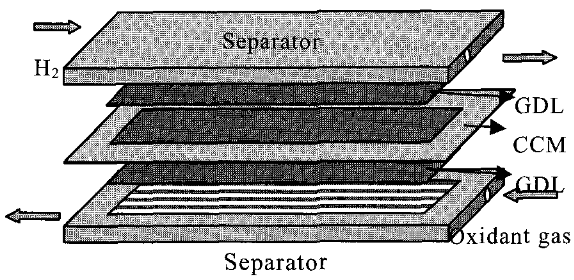

Fig. 1. Cell configuration

IV curve measurement: Conditions of IV curve measurement are shown in Table IV. Schematic diagram of equipment for IV curve measurement is shown in Fig. 2. The Condition of power generation was set at high efficiency which was aimed at automobile application.

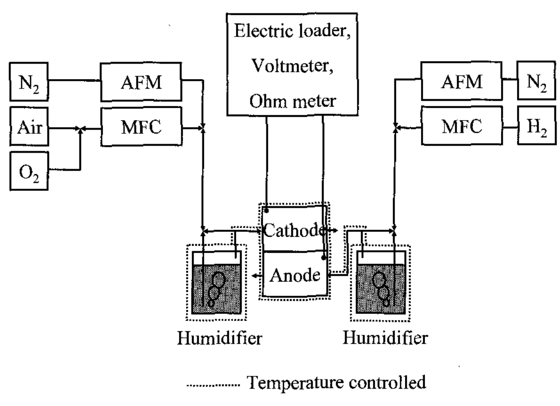

Fig. 2. Schematic diagram of equipment for power generation tests and diagnostic measurements. AFM shows Area flow meter and MFC shows mass flow controller.

Table IV. Conditions of IV measurement

Operation pressure			Ambient pressure	
Cell temperature			80℃	
Humidification temperature			70℃	
Gas composition	Fuel	Oxidant	H$_2$	Air
Gas utilization			70%	70%
Current density(Sweep rate)			0~1.84A/cm^2(5A/min)	

Vacuum impregnation GDL with water: The relations between structure or wettability and the water content of GDL by vacuum impregnation of the water were examined by measuring weight change between GDL and water impregnated GDL. Water was impregnated to GDL by putting GDL in water-bath which is set in vacuum drier [16]. Pressure was set from -96kPa to atmospheric pressure in gauge. Volume ratio of carbon fiber + binder, PTFE and water were valuated by bulk density of GDL, PTFE content and water content. In this valuation, assuming carbon fiber and binder to be graphite, 2.2g/cm3 which is the density of graphite was used for carbon fiber and binder. The density of PTFE and water were 2.2g/cm3 and 1g/cm3 respectively. Each volume valuated by each weight and density. Void volume was valuated by subtracting volume of carbon fiber, binder and PTFE out of whole volume. And, The water impregnated GDLs which was provided in this way were used for the measurement of dehydration pressure.

Dehydration pressure measurements: Schematic diagram of equipment for dehydration pressure test is shown in Fig. 3.

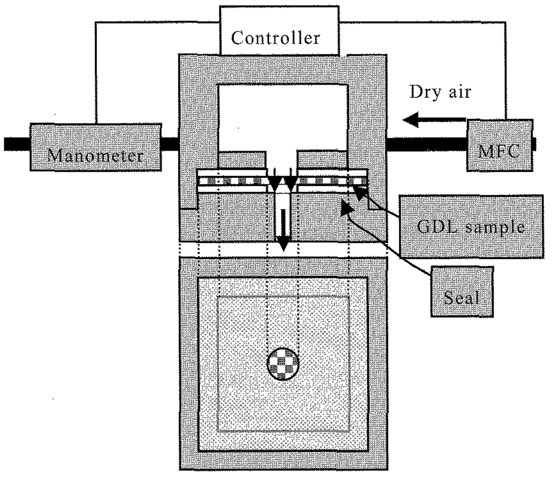

Fig. 3. Schematic diagram of equipment for dehydration pressure test

The differential pressure between the atmosphere and internal pressure of the case can be measured by manometer. One side of this case is connected to mass flow controller and the other side is open.

Water impregnated GDL was set at the open side and boarded in Teflon seat and aluminum board with through-hole 1cm in diameter.

The gas flows from inside of the case to outside through GDL. Internal pressure of the case is increased by permeation resistance of GDL. The differential pressure between the atmosphere and the internal pressure of the case was measured by stepping flow rate after a certain period of time. The first declining point was defined as dehydration pressure.

2.3 Determination of limiting current

The limiting current density $i_{\lim}$ is representative of the oxygen transport limitation on the cathode. $i_{\lim}$ was determined through approximating experimental value of IV curves with equation (1) by least-square method. [17-19]

$$E_{IR} = E_0 - b\ln\left(\frac{i}{i_0}\right) - d\ln\left(\frac{i_{\lim}}{i_{\lim}-i}\right) \quad (1)$$

$$E_{IR} = E + iR \quad (2)$$

i is current density. The parameters for approximation are b, i_0, d and $i_{\lim}$. b and i_0 are called Tafel slope and exchange current density respectively. E_{IR} is IR free cell voltage. Cell voltage E was corrected by cell resistance R which was measured simultaneously with equation (2).

The gas diffusivity was changing as function of current density when significant flooding was caused. IV curve was not given in equation (1). In these cases, $i_{\lim}$ was determined as the current for 0V of the cell voltage through approximating experimental values near $i_{\lim}$ of IV curves by collinear approximation.

The analysis of the IV curves in this study is based on two disregards, negligible anode polarization and insignificant hydrogen crossover.

3. RESULTS AND DISCUSSION

3.1 SEM and AFM images

Images which were observed by SEM and AFM are shown in Fig. 3. Fig. 3 (a) shows GDL which is named as Type D. There were through-holes in Type D. The aim of making through-holes in GDL is to improve the property of liquid water transport. Base material is carbon paper. Fig. 3 (b) shows a GDL which is named as Type E. Type E is carbon felt which contains no binder. Web-like white things were PTFE. Fig. 3 (c-1) and (d-1) show GDLs which are named as Type F and 030-12, respectively. Type F is carbon paper which contains low amount of binder. 030-12 is commercially available carbon paper. Fig. 3 (c-2) and (d-2) show cross section of each GDL. In contrast with binder is closely packed in 030-12, there is lower binder in Type F. Fig. 3 (e-1) and (e-2) show surface of carbon fiber of GDL which is named as Type B and base material, respectively. Type B is hydrophilized by acid treatment. The surface of carbon fiber of Type B has much roughness by comparison with base material. It is inferred that surface roughness of carbon fibers increase wettability of GDL.

3.2 Determination of limiting current with IV curves

Demonstration of limiting current is determined by experimental data of GDL. Fig. 5 shows 2 types of IV curve and each determination. Right one is standard shape which was fitted by equation (1) and left one is anomaly shape which was indicative of flooding of IV curves. Right one was fitted by collinear approximation with last several points.

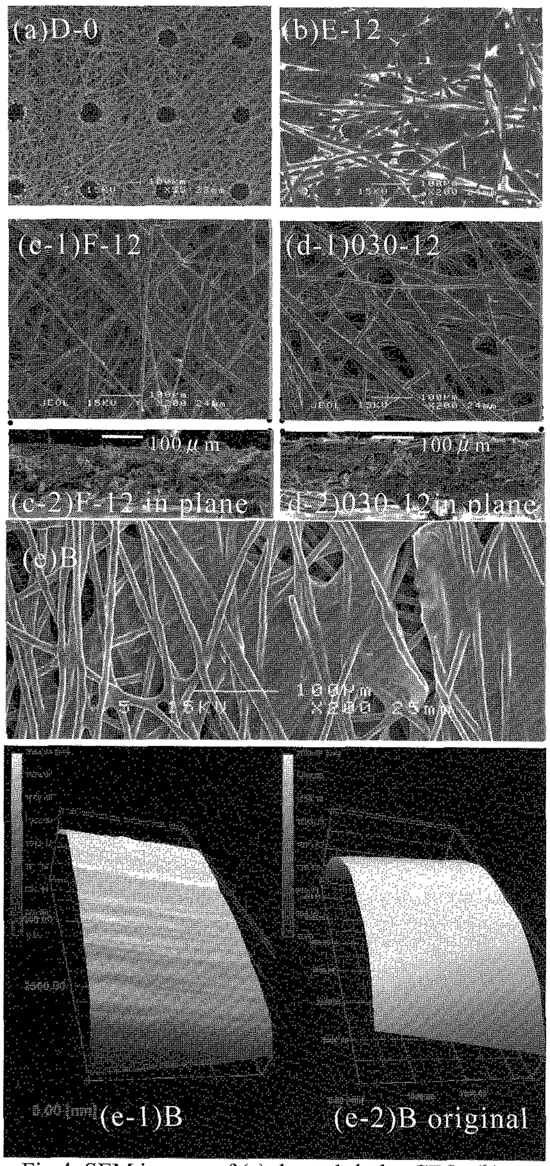

Fig.4. SEM images of (a) through-holes GDL, (b) no binder GDL, (c-1) low amount of binder GDL, (c-2) cross section of (c-1), (d-1) Toray H030 GDL, (d-2) cross section of (d-1), (e) hydrophilic GDL and AFM images of (e-1) surface of carbon fiber of (e), (e-2) original of (e).

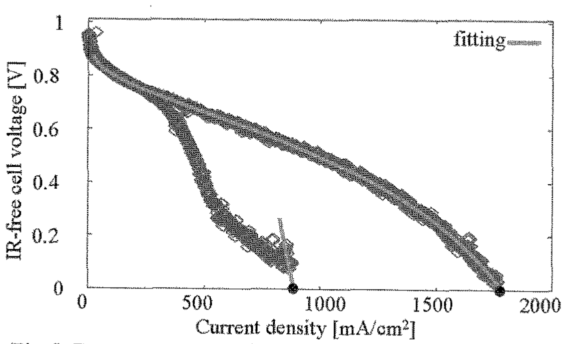

Fig.5. Demonstration of limiting current determination

3.3 Vacuum impregnation GDL with water

Volume ratio of each GDL is shown in Fig. 6. It shows that hydrophobic treated GDL is lower volume water content than no treated GDL. In addition, quite a lot of water was impregnated to no binder GDL E-0 which is carbon felt GDL whose type is E of no treated one. The volume ratio of water was over 1. This is thought to be due to increased volume of GDL because there is no binding among carbon fibers. Furthermore, hydrophobic treated GDL E-12 was also high level of water content. Hydrophilic treated GDL B contended water as same as the other no treated GDL.

Suppose, GDL consists mainly of straight capillary pipes. The relationship among structure, affinities for water and differential pressure ΔP is expressed as next equation [8].

$$\Delta P = \frac{-4\gamma\cos\theta}{D} \tag{3}$$

γ is interfacial tension of water. D is pore diameter. θ is contact angle. On hydrophobic pore of GDL, higher hydrophobicity and smaller pore diameter make pressure of water intrusion larger.

On the other hand, on hydrophilic pore of GDL, higher hydrophilicity and smaller pore diameter make pressure of water absorption larger.

It is suggested that higher capillary pressure makes water content of the GDLs which were treated by PTFE with higher hydrophobicity fewer than neutral GDLs.

Table I shows that Type E which is no binder GDL has smaller bulk density. Therefore, it is suggested that higher capillary pressure makes water content of the GDLs which were treated by PTFE with higher hydrophobicity fewer than neutral GDLs.

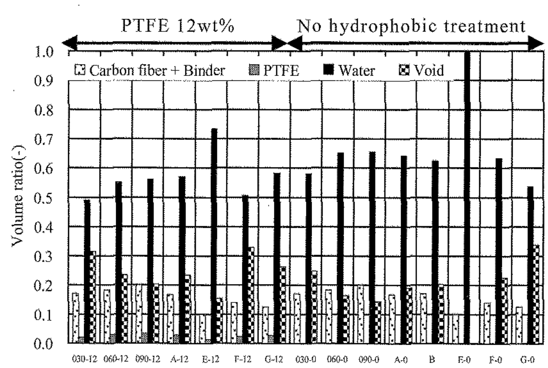

Fig.6. Volume ratio of water impregnated GDLs

3.4 Dehydration pressure

Limiting current expressed as a function of dehydration pressure: The relationship between dehydration pressure and limiting current which is determined at 3.2 is shown in Fig. 7. The smaller the dehydration pressure is, the greater the limiting current becomes. Strong correlation exists when the limiting current is expressed as a function of dehydration pressure. This suggests that the property of water transport of GDL as dehydration pressure dominates resistively of flooding in GDL, strongly.

Furthermore, the property of water transport of GDL is dominated by the amount of binder, the affinities of carbon fiber for water and the complexity of pathway of water. It suggests that resistively of flooding in GDL is improved by making smaller dehydration pressure change in these parameters. Additionally, it is inferred that the driving force of liquid water transport is differential pressure between internal of MEA and gas channel.

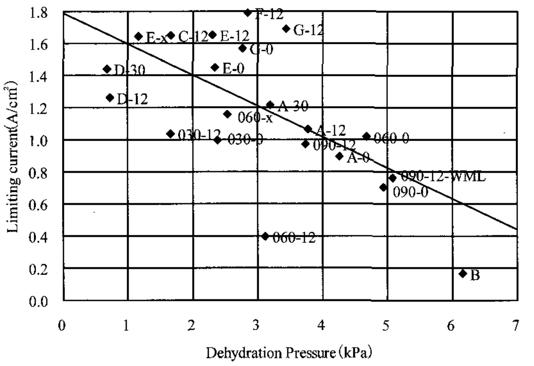

Fig. 7. Limiting current as function of dehydration pressure

Influence of area and intervals of through-holes: One of the easiest ways to decrease dehydration pressure significantly is to make bigger through-holes. It is found that D-12 is the lowest dehydration pressure. However C-12 is the highest dehydration pressure compared A-12 which has no through-hole, C-12 and D-12 which have through-holes 90μm and 184μm in diameter, respectively, at intervals of 700μm. This fact suggests that bigger through-holes make dehydrate water better, on the other hand, decreasing gas permeable area might be caused by flooding in through-holes. It suggests that optimization of area of thorough-holes is important.

Influence of WML: Limiting current of the GDL with WML which is for low humidity operation is low. It is inferred that flooding is caused by significantly small pore size of carbon black. Therefore, for instance, it is necessary to enhance the performance of GDL for all range of humidity that GDL has not only WML but also through-hole.

Influence of hydrophilicity: Limiting current is the smallest and dehydration pressure is the highest for hydrophilic GDL Type B. It would appear that interaction between water and carbon fiber is higher than neutral one.

Characteristics of high performance GDL for flooding: The dehydration pressure of the group of GDLs of which limiting current is over 1.6A/cm2 is in range from 1.5kPa to 4kPa. All GDLs are to aim at decreasing dehydration pressure by enlarging pore diameter and simplifying pathway of water.

On the other hand, limiting currents of 030-12, 030-0, 060-x and 060-12 are about 0.5A/cm^2 to 1A/cm^2. Those limiting currents are smaller than those GDLs despite in same range of dehydration pressure.

These GDLs are high bulk density and high amount of binder, so it is inferred that the property of water transport in plane decreases. Despite of 090-12, 090-0 of which bulk is as same as 030-12, 030-0, 060-x and 060-12, limiting current of thinner GDLs is smaller than thicker GDLs. This also indicates of the property of water transport in plane.

4. CONCLUSION

Resistively of flooding of various sorts of types of GDLs are investigated by power generation test. As the examination outside of the cell, the property of liquid water transport was evaluated by measuring dehydration pressure of through plane direction from water impregnated GDL. The conclusions provided from those results are shown below.

1 Strong negative correlation existed between flooding phenomena in the GDL and pressure to dehydrate from the GDL.

2 It is proposed that expanding pore diameter to certain point and simplifying pathway of water by reducing binder and making through-holes on hydrophobic treated GDL are effective against the flooding phenomena.

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