



저작자표시-동일조건변경허락 2.0 대한민국

이용자는 아래의 조건을 따르는 경우에 한하여 자유롭게

- 이 저작물을 복제, 배포, 전송, 전시, 공연 및 방송할 수 있습니다.
- 이차적 저작물을 작성할 수 있습니다.
- 이 저작물을 영리 목적으로 이용할 수 있습니다.

다음과 같은 조건을 따라야 합니다:



저작자표시. 귀하는 원저작자를 표시하여야 합니다.



동일조건변경허락. 귀하가 이 저작물을 개작, 변형 또는 가공했을 경우에는, 이 저작물과 동일한 이용허락조건하에서만 배포할 수 있습니다.

- 귀하는, 이 저작물의 재이용이나 배포의 경우, 이 저작물에 적용된 이용허락조건을 명확하게 나타내어야 합니다.
- 저작권자로부터 별도의 허가를 받으면 이러한 조건들은 적용되지 않습니다.

저작권법에 따른 이용자의 권리는 위의 내용에 의하여 영향을 받지 않습니다.

이것은 [이용허락규약\(Legal Code\)](#)을 이해하기 쉽게 요약한 것입니다.

[Disclaimer](#)

공학석사 학위논문

Single cell characteristics of  
high temperature polymer  
electrolyte membrane fuel cell  
under low humidity conditions

고온 저가습에서의 고분자 전해질막  
연료전지 단위전지의 운전 특성 연구

2012 년 8 월

서울대학교 대학원

공과대학 화학생물공학부

조민경

Single cell characteristics of  
high temperature polymer  
electrolyte membrane fuel cell  
under low humidity conditions

고온 저가습에서의 고분자 전해질막  
연료전지 단위전지의 운전 특성 연구

지도 교수 성영은

이 논문을 공학석사 학위논문으로 제출함  
2012 년 8 월

서울대학교 대학원  
공과대학 화학생물공학부  
조민경

조민경의 공학석사 학위논문을 인준함  
2012 년 8 월

위 원 장 \_\_\_\_\_ 오승모 (인)

부위원장 \_\_\_\_\_ 성영은 (인)

위 원 \_\_\_\_\_ Nicola Pinna (인)

## **Abstract**

# **Single cell characteristics of high temperature polymer electrolyte membrane fuel cell under low humidity conditions**

Min Kyung Cho

The Graduate School of Chemical & Biological Engineering

Seoul National University

The study of PEMFC operation at high temperature (120 °C) (HT-PEMFC) under low humidified condition remains challenging with improving chemical and electrochemical stability while maintaining high proton conductivity. Therefore, it is in the early stage of development. In this paper, optimization of fuel cell operating conditions and establishment of the electrochemical characterization technique were performed to evaluate the developed membrane. The performance decay during 40 h has been decreased from 12.0% to 2.78% and durability was improved by almost 2 times which was from 60 hours to more than 100 hours through applying low porous gas diffusion layer (GDL). Moreover, real-time ohmic resistances were collected by introducing

galvanostatic electrochemical impedance spectroscopy at high frequency (1 kHz) to investigate the effect of inlet relative humidity on the performance of HT-PEMFCs. Produced water during the cell operation, enhances the performance by improving proton conductivity. Ohmic resistance ( $R_{ohm}$ ) was inversely proportional to the relative humidity and the membrane dehydration was the main factor for the cell performance degradation.

**Keywords :** Polymer electrolyte membrane fuel cell, high temperature, low relative humidity, proton conductivity, gas diffusion layer

**Student number :** 2010-24103

# Contents

<b>Chapter 1. Introduction .....</b>	<b>1</b>
1.1 Fuel cells.....	2
1.1.1 Backgrounds and principles of fuel cells.....	2
1.1.2 Classification and applications of fuel cells.....	5
1.2 High temperature PEMFCs (HT-PEMFCs).....	8
1.3 Concept of study.....	10
<b>Chapter 2. Experimental .....</b>	<b>11</b>
2.1 Preparation of membrane .....	11
2.2 Fabrication of membrane electrode assemblies (MEAs) .....	14
2.3 Single cell operation.....	15
2.4 Electrochemical characterization .....	18
<b>Chapter 3. Results and discussion .....</b>	<b>19</b>
3.1 Optimization of operating conditions .....	19
3.2 Establishment of evaluation techniques .....	23
3.3 Electrochemical characterization .....	27
<b>Chapter 4. Conclusion.....</b>	<b>44</b>
<b>References .....</b>	<b>45</b>
<b>초    록 .....</b>	<b>48</b>

## **List of Tables**

Table 1. Fuel cell types .....	6
Table 2. Fuel cell applications, pros and cons .....	7

## List of Figures

Figure 1	Schematic of a PEM fuel cell .....	4
Figure 2	Chemical structure of PES 70 .....	12
Figure 3	Preparation method of sulfonated poly(ether sulfone) based silica nanocomposite membranes .....	13
Figure 4	Components of a single cell .....	16
Figure 5	Cell operation with varying RHs of 10%, 20% and 35% .....	17
Figure 6	Partial pressure of air and water vapor at atmospheric pressure and with back pressure at 120 °C .....	19
Figure 7	The cell performance of MEAs with GDL 10 BC and 34 BC .....	22
Figure 8	Chemical structures of perfluorinated polymer electrolyte membrane .....	24
Figure 9	A schematic representation of the first proton hopping at the surface of Nafion before and after first jump .....	25
Figure 10	OCV changes with time at high temperature under low humidified cell operation.....	26
Figure 11	Cell performance with varying RHs (10%, 20% and 35%) ...	29
Figure 12	Polarization curves of Nafion MEA with RHs of 10%, 20% and 35% .....	30
Figure 13	Real-time ohmic resistances of Nafion MEA at RHs of 10%, 20% and 35%.....	31
Figure 14	Experimental profile for evaluation of PES70_S05 .....	33
Figure 15	Performance of PES70_S05 MEA at 120 °C , RH of 35%.....	36
Figure 16	Polarization curves of PES70_S05 MEA at 0 h, 1 h, and 3.5 h.....	37
Figure 17	Real-time ohmic resistances of PES70_S05 MEA at RH of 35% .....	40

Figure 18	Proton conductivity of PES70_S05.....	41
Figure 19	Comparison of $\Delta E$ and $\Delta iR$ drop of PES70_S05 MEA .....	42
Figure 20	Proton conductivity of Nafion membrane and PES70_S05 with RHs.....	43

# 1. Introduction

With the successful industrial development and economic growth, the standards of living and quality of life have been greatly improved; however, pollution and depletion of natural resources came along with the development. Pollution and depletion of natural resources are the well-known world's biggest problems. For these reasons, sustainable and renewable energy becomes a public interest in electricity generation from unlimited sources while keeping the earth green. Hydrogen is not a primary energy source like coal and gas. Hydrogen is a secondary energy like electricity which is produced from available primary energy, and also this abundant source is environmentally and climatically clean. Hydrogen can be used as fuel in the fuel cells to generate electricity. Therefore, hydrogen and fuel cells are getting attention as the solution of the energy challenge [1, 2] .

## 1.1 Fuel cells

### 1.1.1 Backgrounds and principles of fuel cells

Fuel cell technologies have received much attention due to the growing concerns on the depletion of fossil fuel based energy resources and climate changes. Fuel cells are electrochemical devices that directly convert chemical energy stored in fuels such as hydrogen to electrical energy as shown in Fig. 1. Their efficacies are high and emissions are low. The efficiency can reach as high as 60% in electrical energy conversion and overall 80% in co-generation of electrical and thermal energies with higher than 90% reduction in major pollutants [3]. The first fuel cell was invented by Sir William Robert Grove, who was an English lawyer and scientist. The cell worked with hydrogen as its fuel, thus demonstrating the ability to generate electric current through direct conversion of the fuel's chemical energy. In other words, the fuel cell is the electrochemical system that continuously converts chemical energy into electric energy as long as fuels are supplied. The first commercial use of fuel cells was in NASA space for generating power for probes of satellite and space capsules. After that, fuel cells have been developed for commercial, industrial and residential primary and backup power generation [4].

Fuel cells are open systems where the anode and cathode are just charge-transfer and the active masses undergoing the redox reaction are supplied from outside the cell, either from the environment (oxygen from air) or from the tank (hydrogen). The reaction takes place inside a structure, consisting

essentially in two electrodes, which are anode and cathode, separated by an electrolyte. In the case of proton exchange fuel cell (PEMFC), the hydrogen at anode is dissociated into proton, in accordance with the oxidation reaction,  $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$ . At the cathode, the oxygen, the electrons and the protons recombine to produce water,  $2\text{H}^+ + 1/2\text{O}_2 + 2\text{e}^- \rightarrow \text{H}_2\text{O}$ . Therefore, the principle of the fuel cell is the conversion of water electrolysis [3].

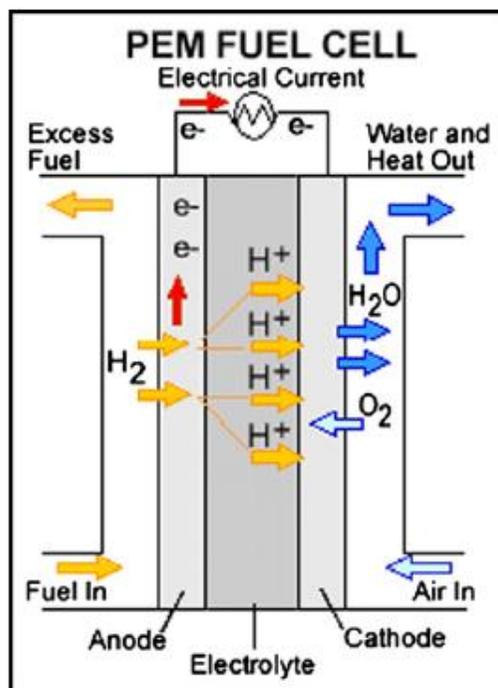


Fig. 1. Schematic of a PEM fuel cell.

### 1.1.2 Classification and applications of fuel cells

Fuel cells are mainly composed of the anode, the electrolyte, and the cathode and can be classified by the electrolyte substance used and operating cell temperature. Various types of fuel cells are under development. Table 1 and 2 describes types of fuel cells and their applications. The working temperature is very important factors in deciding the application and selection of reactant and electrode catalyst [5] . As it is described in the table 1 and 2, fuel cells can be used not only in the stationary applications for power generation of buildings and residences but also in the mobile applications

Table 1. Fuel cell types

Fuel cell type	Common electrolyte	Operating temperature	Typical stack size	Efficiency
Polymer electrolyte membrane (PEM)	Perfluoro sulfonic acid	50 ~100 °C	<1 kW ~100 kW	60% transportation, 35% stationary
Alkaline (AFC)	Aqueous solution of potassium hydroxide soaked in a matrix	90 ~100 °C	10 ~ 100 kW	60%
Phosphoric acid (PAFC)	Phosphoric acid soaked in a matrix	150~200 °C	400 kW 100 kW module	40%
Molten carbonate (MCFC)	Solution of lithium, sodium, and/or potassium carbonates, soaked in a matrix	600 ~ 700 °C	300 kW ~3 MW 300 kW module	45 ~ 50%
Solid oxide (SOFC)	Yttria stabilized zirconia	700 ~ 1000 °C	1 kW ~ 2 MW	60%

Table 2. Fuel cell applications, pros and cons

Fuel cell type	Applications	Pros	Cons
Polymer electrolyte membrane (PEM)	<ul style="list-style-type: none"> <li>-Backup power</li> <li>-Portable power</li> <li>-Transportation</li> <li>-Specialty vehicles</li> </ul>	<ul style="list-style-type: none"> <li>-Solid electrolyte reduces corrosion &amp; electrolyte management problems</li> <li>-Low temperature</li> <li>-Quick start up</li> </ul>	<ul style="list-style-type: none"> <li>-Expensive catalysts</li> <li>-Sensitive to fuel impurities</li> <li>-Low temperature waste heat</li> </ul>
Alkaline (AFC)	<ul style="list-style-type: none"> <li>-Military</li> <li>-Space</li> </ul>	<ul style="list-style-type: none"> <li>-Cathode reaction faster in alkaline electrolyte, leads to high performance</li> <li>-Low cost components</li> </ul>	<ul style="list-style-type: none"> <li>-Sensitive to CO<sub>2</sub></li> <li>-Electrolyte management</li> </ul>
Phosphoric acid (PAFC)	<ul style="list-style-type: none"> <li>-Distributed generation</li> </ul>	<ul style="list-style-type: none"> <li>-Higher temperature enables CHP</li> <li>-increased tolerance to fuel impurities</li> </ul>	<ul style="list-style-type: none"> <li>-Pt catalyst</li> <li>-Long start up time</li> <li>-Low current and power</li> </ul>
Molten carbonate (MCFC)	<ul style="list-style-type: none"> <li>-Electric utility</li> <li>-Distributed generation</li> </ul>	<ul style="list-style-type: none"> <li>-High efficiency</li> <li>-Fuel flexibility</li> <li>-Various catalysts</li> <li>-Suitable for CHP</li> </ul>	<ul style="list-style-type: none"> <li>-High temperature corrosion and breakdown</li> <li>-Long start up time</li> <li>-Low power density</li> </ul>
Solid oxide (SOFC)	<ul style="list-style-type: none"> <li>-Auxiliary power</li> <li>-Electric utility</li> <li>-Distributed generation</li> </ul>	<ul style="list-style-type: none"> <li>-High efficiency</li> <li>-Fuel flexibility</li> <li>-Various catalysts</li> <li>-Solid electrolyte</li> <li>-Suitable for CHP&amp;CHHP</li> <li>-Hybrid/GT cycle</li> </ul>	<ul style="list-style-type: none"> <li>-High temperature corrosion and breakdown of cell components</li> <li>-High temperature operation requires long start up time and limits</li> </ul>

## 1.2 High temperature PEMFCs (HT-PEMFCs)

The recent studies are focused on the development of polymer electrolyte for HT-PEMFC ( $> 100\text{ }^{\circ}\text{C}$ ) applications due to the fast electrode kinetics, simple thermal and water management, heat utilization, high CO tolerance. The most commonly used proton exchange membrane, Nafion, is no longer suitable in the HT-PEMFC under low humidity operation since Nafion relies on liquid water for humidification of the membrane to transport proton and also its glass transition temperature is approximately  $110\text{ }^{\circ}\text{C}$ . For the high temperature application, the polymer should have high glass transition temperatures with sufficient proton conductivity. In the current state, there are some technical issues with the high temperature treatment of polymer electrolyte membranes. Polymer membranes are incapable of operating at high temperatures due to the water evaporation from the membrane which will result in a loss of proton conductivity. High proton conductivity is required to achieve a high power density in fuel cells. Therefore, the developed membrane for HT-PEMFC application requires the followings. First, the material cost should be low. Secondly, high proton conductivity should be achieved above  $100\text{ }^{\circ}\text{C}$ . Third, water uptake should be moderate. Lastly, the membrane should provide long life time. High temperature membranes currently under development can be classified into modified perfluorosulphonic acid (PFSA) membranes, membranes based on partially fluorinated and aromatic hydrocarbon polymers, inorganic-organic composites, and acid-base polymer membranes. Amongst them, the acid base polymer membrane, phosphoric acid doped polybenzimidazole (PBI) was

reported as one of the most promising membrane for the HT-PEMFC applications [6, 7] . However, leaching of phosphoric acid during the cell operation cannot be ignored since it causes the degradation of the bipolar plate and contamination of the gas outlet.

It is true that development of the membrane is important to achieve the expected advantages, but the cell operating conditions and characterization techniques are also needed to be studied and optimized for the HT-PEMFC evaluation with the developed materials.

### **1.3 Concept of study**

This paper investigates the characteristics of HT-PEMFCs under low humidified conditions. In the case of HT-PEMFC (120 °C) operation, maintaining the hydration level inside the system is crucial and modification of the operating conditions are needed such as requirement of back pressure to maintain membrane hydration. Also, applying low porosity gas diffusion layer (GDL) is expected to reduce the water evaporation rate from the system. Since the study of HT-PEMFC is in very early stage, effective and reliable evaluation techniques for developed membrane are needed to be achieved. By modifying the cell operating conditions, the performance of PEMFC operating at 120 °C under low humidity will be enhanced. Moreover, establishment of effective evaluation techniques to monitor the developed membranes for HT-PEMFC applications will be required.

## 2. Experimental

### 2.1 Preparation of membrane

#### *70 mol% sulfonated poly(ether sulfone) silica nanocomposite membranes*

– The sulfonated poly(ether sulfone) silica nanocomposite membrane was provided by Krishnan, N.N. The synthesis of 70 mol% sulfonated poly(ether sulfone) with the chemical structure presented in Fig. 2 was carried out as in the paper written by Krishnan, N.N. [8]. After the polymer was ready, silica nanocomposite membranes were prepared by optimized procedure shown in Fig. 3. Briefly, the potassium salt from cast solutions were prepared by dissolving the fibrous copolymers in DMAc and filtered with 0.45  $\mu\text{m}$  Teflon<sup>TM</sup> syringe filter. A known amount of polymer casting solution was transferred to a ball milling container containing ZrO<sub>2</sub> balls of 5 mm diameter each. Then 5% (based on polymer) silica was added to the same container to synthesize 5% silica nanocomposite membrane. The ball milling speed levels were adjusted to obtain the well-dispersed silica nanoparticles based cast solution. After that, the solution was poured onto a clean glass plate and casted immediately. The salt form membrane was acidified with 1 N HCl solution for 48 h at room temperature. The acid form membranes were washed several times with deionized water until a neutral pH of the washing water was achieved. Lastly, the acid form membranes were stored in deionized water at room temperature [9].

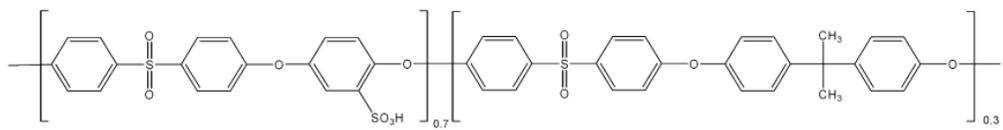


Fig. 2 Chemical structure of PES70 [9].

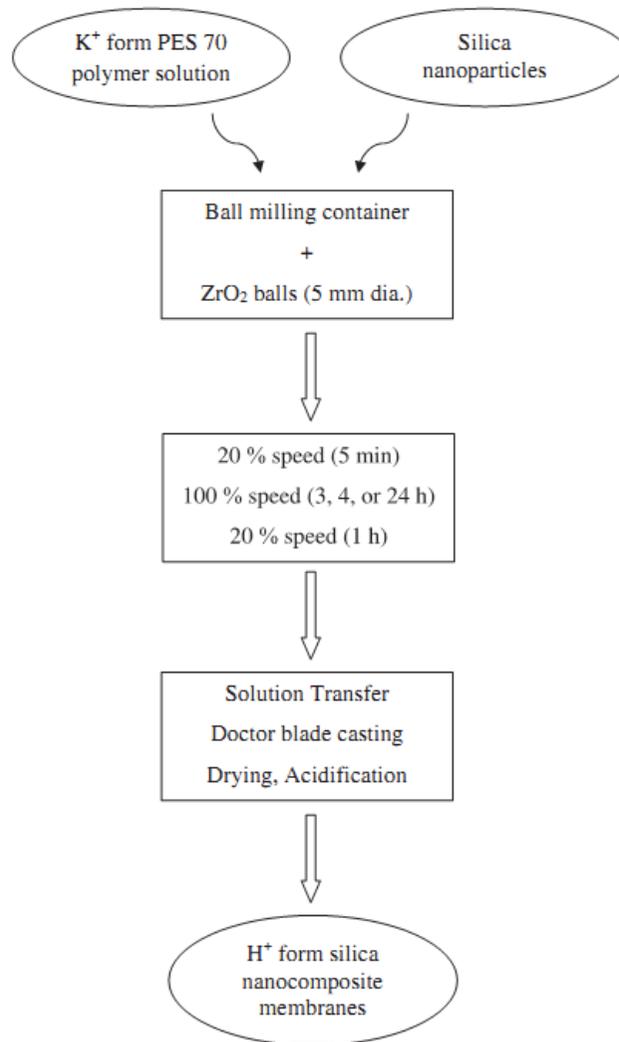


Fig. 3 Preparation method of sulfonated poly(ether sulfone) based silica nanocomposite membranes [9].

## 2.2 Fabrication of membrane electrode assemblies (MEAs)

Commercial Nafion MEAs (M815, Gore<sup>TM</sup>) and lab fabricated MEAs were used in this experiment. The lab fabricated MEAs were made by catalyst coated membrane (CCM) method using the sulfonated poly (ether sulfone)-based silica nanocomposite membranes provided by N.N. Krishnan. The MEAs were loaded with  $0.4 \text{ mg cm}^{-2}$  of Pt on both cathode and anode side by using the auto spray machine. The active electrode area was designed to  $10.24 \text{ cm}^2$ . The catalyst ink slurry was prepared by mixing a carbon-supported platinum catalyst (45.6 wt% Pt/C, Tanaka K.K.), isopropyl alcohol (Burdick and Jackson) and 5 wt% Nafion<sup>®</sup> ionomer (EW1100, Dupont Inc.). After 4 h of ultrasonification, the catalyst ink was coated on the sulfonated poly (ether sulfone)-based silica nanocomposite membrane. Then, the MEA was dried at  $60 \text{ }^\circ\text{C}$  for 45 min.

## 2.3 Single cell operation

The prepared MEAs were assembled in a custom-made single cell frame with gas diffusion media (Sigracet 10 BC or 34 BC, SGL Carbon Inc.) and Teflon<sup>®</sup> gaskets as shown in Fig. 4. The cell was operated at 120 °C with controlled back pressure of 1.2 bars. The hydrogen and gas fluxes were fixed at 1.5 and 2 times the stoichiometry at a current density of 0.4 A cm<sup>-2</sup>, respectively. After the cell was activated with constant current operation at 0.2 A cm<sup>-2</sup>, electrochemical characterizations were carried out using a high current potentiostat/galvanostat (HCP-803, BioLogic). The cell operation with commercial Nafion MEA was carried out at three different inlet relative humidities (RHs), 10, 20 and 35%, controlled by a temperature of humidifier corresponding to the required relative humidity. Fig. 5 represents the cell operation procedure. As presented in Fig. 5 schematically, both the commercial Nafion MEA and PES70\_S05 were initially activated at 0.2 A cm<sup>-2</sup> under 120 °C, RH of 35% for 8 hours, and i-V measurements were performed. Then, RH of cathode and anode were decreased to 20%, the single cell was stabilized for 1.5 hours at constant current of 0.2 A cm<sup>-2</sup>, and i-V measurements were carried out. The same stabilization method and i-V measurements were repeated at RH of 10% and also with the increase of RH to 20% and 35%. During the constant current operation, ohmic resistance was obtained every 2 minutes by employing galvanostatic electrochemical impedance spectroscopy (GEIS). Since boiling temperature of water is 100 °C, the maximum humidifier temperature was set up around 90 °C which corresponds to RH of 35%.

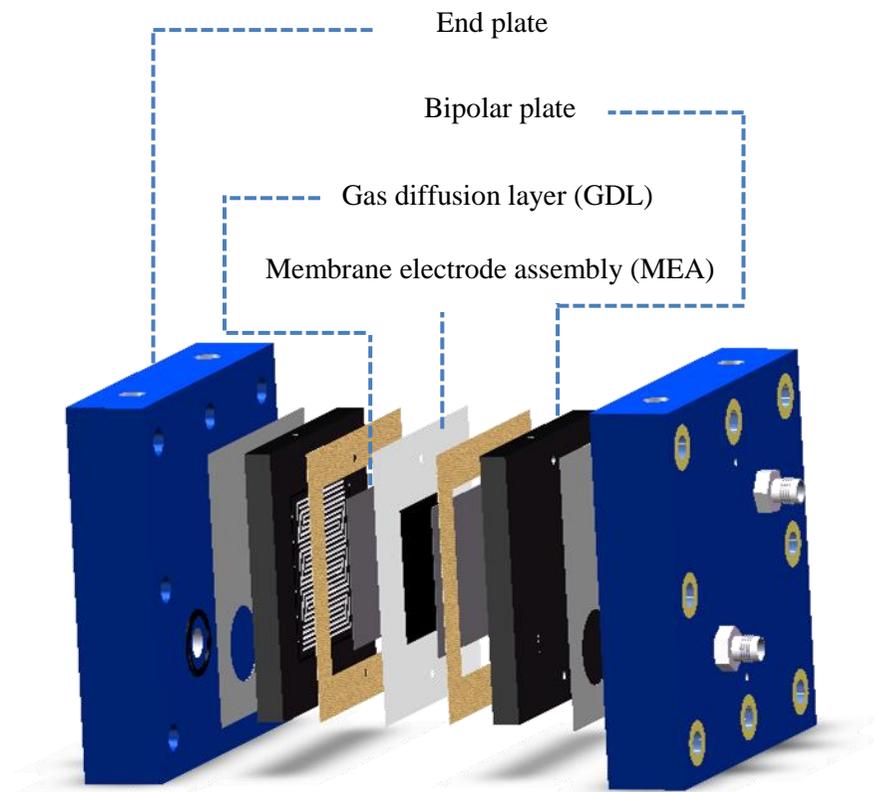


Fig. 4 Components of a single cell.

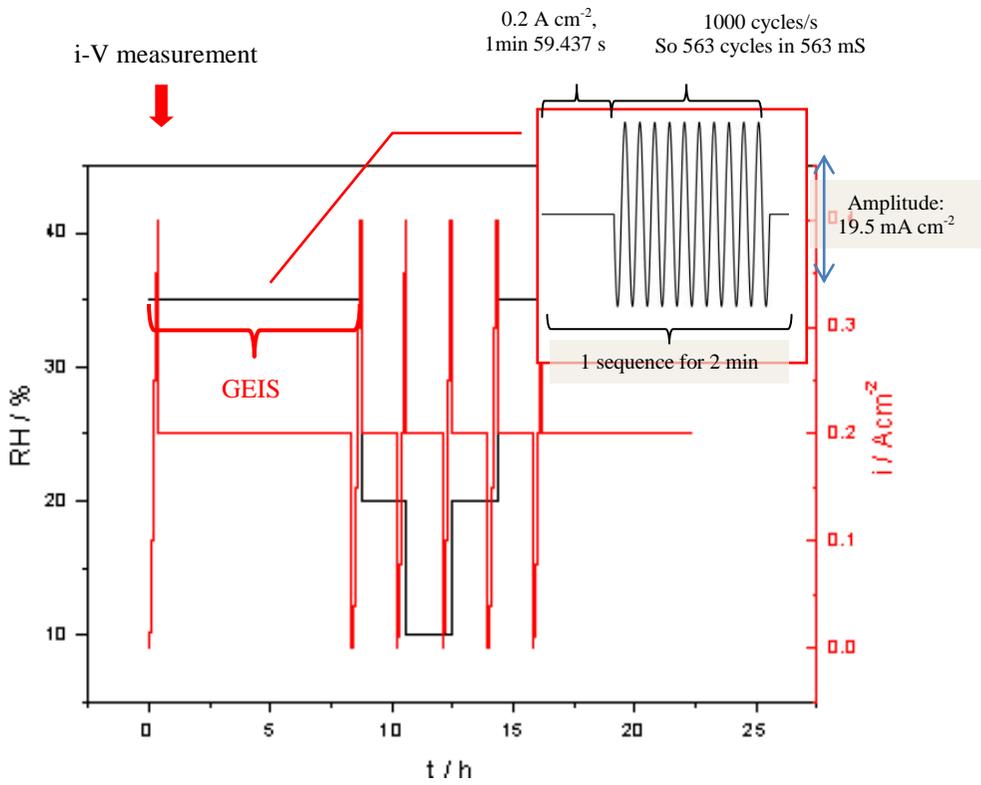


Fig. 5 Cell operation with varying RHs of 10%, 20% and 35%.

## 2.4 Electrochemical characterization

The MEAs were analyzed electrochemically after the activation step. In the experiment with varying relative humidities (10%, 20% and 35%), measurements of polarization curve performed using the potentiostat / galvanostat (HCP-803, BioLogic) after the system was stabilized with the changed relative humidities in order to establish the dependence of the cell performance on relative humidity. To correlate the performance degradation and electrochemical characteristics of the single cell as a function of the cathode inlet relative humidity, ac impedance measurements at high frequency were performed. Also, in the experiment for evaluating developed membrane (PES70\_S05), ac impedance measurements at high frequency were performed to investigate the behavior of the membrane at high temperature with low humidified conditions.

Electrochemical impedance spectroscopy (EIS) at high frequency was performed every 2 minutes to monitor the changes in ohmic resistances ( $R_{ohm}$ ) as the relative humidity was adjusted. The cathode (Air) was used as a working electrode, whereas the anode (hydrogen) served as counter and the reference electrode. The ac frequency was fixed at 1 kHz to monitor the  $R_{ohm}$ . The amplitude of the sinusoidal current signal was  $19.5 \text{ mA cm}^{-2}$  at an applied current of  $0.2 \text{ A cm}^{-2}$ .

### 3. Results and discussion

#### 3.1 Optimization of operating conditions

Cell operating conditions used in low temperature PEMFC could be unfavorable for the HT-PEMFC operation. For example, HT-PEMFC operation requires pressure to maintain membrane hydration, which is needed for proton transport [8]. Fig. 6 shows the partial pressure of water vapor and gases of humidified condition at the atmospheric pressure and with the back pressure. As shown in Fig. 6, without back pressure applied ( $P_{\text{total}} = 1 \text{ atm}$ ), gas cannot exist other than vapor since water exists as vapor and take all of the volume. As the back pressure is applied, the partial pressure of gas increases. In other words, sufficient  $\text{H}_2$  and air for electrochemical reaction can be achieved by applying back pressure at above  $100 \text{ }^\circ\text{C}$  with humidified condition. Therefore, the back pressure, 1.2 bars, was applied.

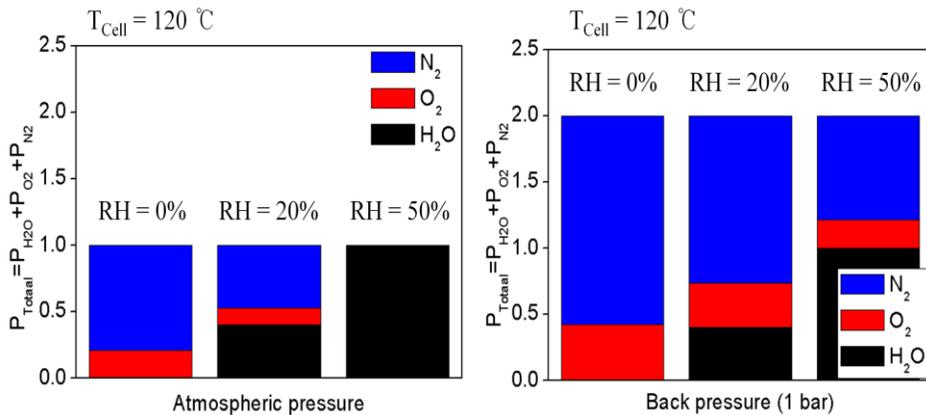


Fig. 6 Partial pressure of air and water vapor at atmospheric pressure and with back pressure condition at  $120 \text{ }^\circ\text{C}$ .

The gas diffusion layer (GDL) in a PEMFC has important roles such as distributing the reactants along the active surface of the electrodes, ensuring proper transport of reactants, product water, electrons, and heat of the reactions [10]. Since flooding in the system is one of the main factors causing the performance decay, GDL has been developed to avoid the flooding issue in the operation of PEMFC at low temperature, fully humidified conditions. However, in the operation of HT-PEMFC under low humidity, membrane dehydration is issued. To enhance water content inside the system, GDL with lower porosity was introduced. The commercial GDL 10 BC with 82% porosity and GDL 34 BC with 75% porosity were applied and operated at 0.2 A cm<sup>-2</sup>, 120 °C with 50% and 40% of RH, respectively. The cell performance at constant current operation of 0.2 A cm<sup>-2</sup> of MEAs with different porosities of GDLs, which has the porosity of 75% and 82% for 34 BC and 10 BC respectively, were plotted in Fig. 7. As shown in the figure, even though the MEA with GDL 34 BC was operated at lower humidity, which was relative humidity of 40% while that with GDL 10 BC was relative humidity of 50%, higher performance and durability were achieved. Between 20 h and 60 h, the performance of MEA with 10 BC and 34 BC were decreased from 0.749 V to 0.659 V and 0.790 V to 0.768 V, which were 12.0% and 2.78% of the performance reduction. Rapid degradation after 60 hours of cell operation was observed in the MEA with GDL 10 BC while the durability of the MEA with GDL 34 BC was longer than 100 hours. Low humidity condition is one of the severe environment constraints, which can have strong impacts on the lifetime and reliability of fuel cell systems by decreasing the membrane mechanical

stability [11]. Through this experiment, the cell performance and durability has been improved by applying GDL 34BC which had the lower porosity compared to the commercially used GDL in the low temperature PEMFC application. Therefore, GDL 34BC is more suitable for the HT-PEMFC operation compared to GDL 10BC and it is used in the following HT-PEMFC experiments.

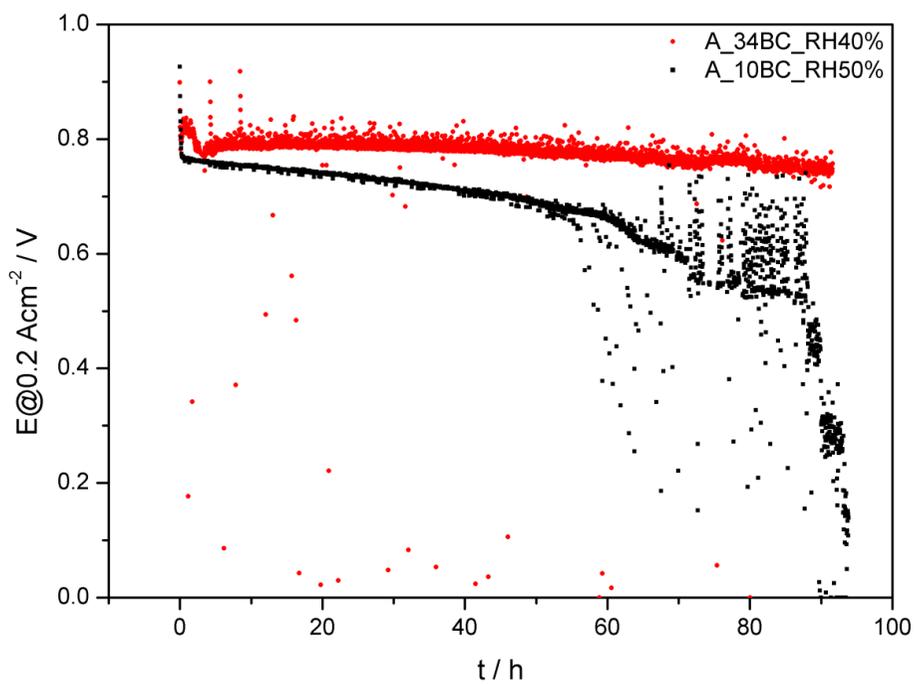


Fig. 7 The cell performance of MEAs with GDL 10 BC and 34 BC.

## 3.2 Establishment of evaluation techniques

The commercial Nafion MEA used in this experiment has the perfluorosulfonic acid membrane. This membrane has the chemical structure as shown in Fig. 8. Water molecules have very important roles in transferring proton through the sulfonic acid sites. Fig 9 displays a schematic representation of the surface hopping of a proton by means of series of hops between adjacent sulfonic acid sites. Since the distance between the ionic groups is too large (0.6~1.2 nm) for a proton to step directly from one  $\text{SO}^{3-}$  to the next, it must hop via intermediate water molecules [12]. Therefore, the performance of the Nafion MEA is sensitive to humidity level. However, in HT-PEMFC operation, the cell is operated at low humidified conditions which would affect the proton conductivity. Open circuit voltage (OCV) corresponds to the condition of the membrane. To see the OCV change, OCV values were collected for 4000 s as shown in Fig. 10. From the figure, the rapid decrease in OCV values were observed during the first 250 s which represents that if the cell operation is stopped constant current operation to carry on other electrochemical characterization, the results can be affected by the decreased water contents inside the system. This would be also applied to the developed membrane with sulfonic acid sites for proton transport. Therefore, galvanostatic electrochemical impedance spectroscopy (GEIS) is introduced to study the membrane behavior and carried out at  $0.2 \text{ A cm}^{-2}$ , 1 kHz to maintain the constant water production. Through this technique, both performance and  $R_{\text{ohm}}$  can be monitored during the cell operation effectively.

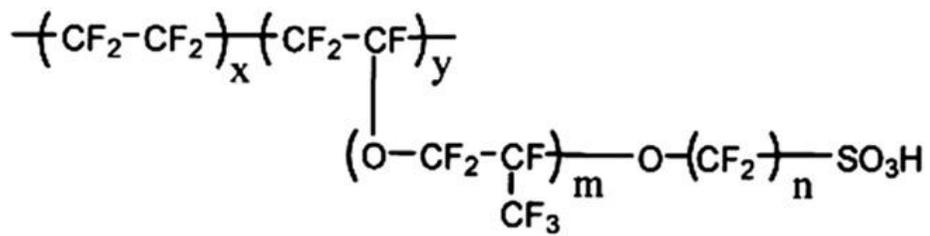


Fig. 8 Chemical structures of perfluorinated polymer electrolyte membrane.

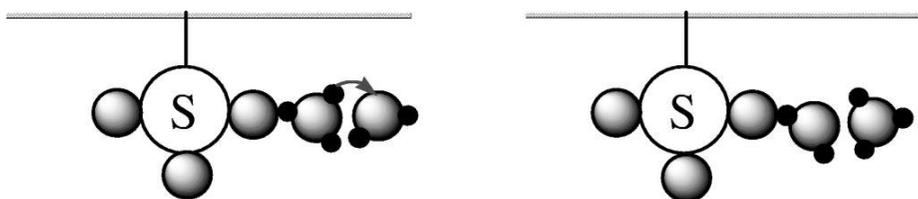


Fig. 9 A schematic representation of the first proton hopping at the surface of Nafion before and after first jump.

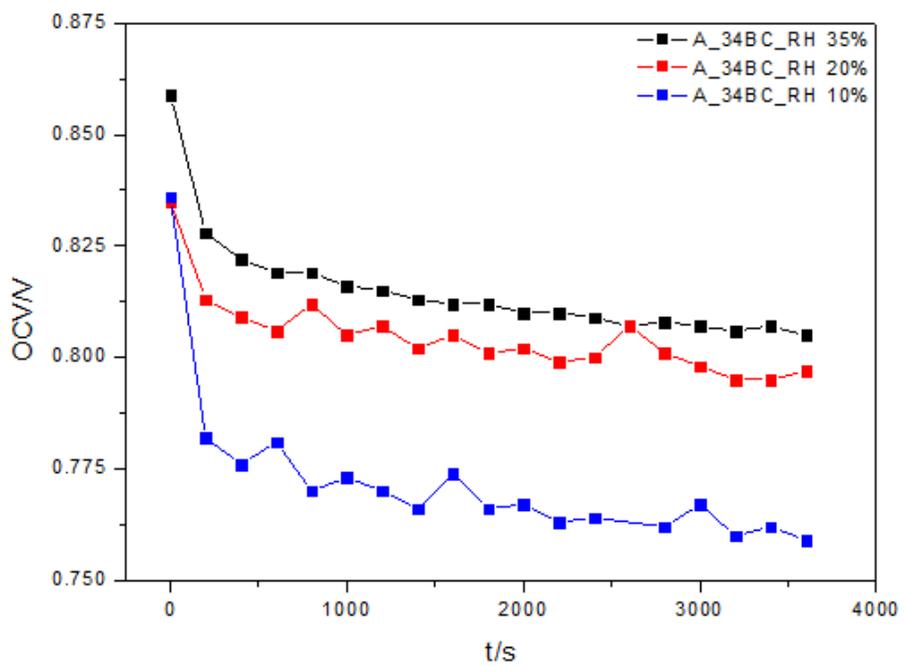


Fig. 10 OCV changes with time at high temperature under low humidified cell operation.

### 3.3 Electrochemical characterization

*Commercial Nafion MEA* - Electrochemical analyses were carried out to further elucidate the effect of the inlet relative humidity on the degradation behaviors of PEMFCs during the cell operation at high temperature under low humidified conditions. Performance and i-V measurements at RHs of 10%, 20% and 35% were obtained to study the dependence of performance on the inlet relative humidity. The EIS at 1 kHz was performed to investigate the effect of the inlet relative humidity on ohmic resistance ( $R_{ohm}$ ) of the MEAs.

To confirm the reliability of GEIS, the commercial Nafion MEA (M815, Gore™) was tested before testing the developed membrane. By controlling relative humidities of the cathode and anode inlet to 10%, 20% and 35%, the characteristics of HT-PEMFC was studied. The cell performance at  $0.2 \text{ A cm}^{-2}$  and i-V at different relative humidities have been plotted in Fig. 11 and 12. As shown in Fig. 11, the cell performance was influenced by relative humidity. The cell performance decreased as reducing the relative humidity of the inlet gases and improved as increasing the relative humidity. In the polarization plot, Fig. 12, the cell voltage at a given current density consistently decreased with the decreasing inlet relative humidities. To evaluate the cell performances, the current density at  $0.2 \text{ A cm}^{-2}$  was selected and the performance obtained with the decreasing inlet relative humidity, 0.743 V and 0.705 V at relative humidity of 35% and 20%, respectively. With the increasing inlet relative humidity, 0.708 V and 0.747 V were obtained at relative humidity of 20% and 35%, respectively. Therefore, as increasing the

relative humidities, similar performances were obtained.

Real-time ohmic resistance was monitored to investigate the degradation behaviors of PEMFCs during the cell operation at low humidities. Fig. 13 indicates that the ohmic resistances of the single cell were varied with the inlet relative humidity. Highest ohmic resistance was observed at the lowest relative humidity and vice versa which were  $0.341 \Omega \text{ cm}^2$ ,  $0.197 \Omega \text{ cm}^2$  and  $0.134 \Omega \text{ cm}^2$  at relative humidities of 10%, 20% and 35%, respectively. Ohmic resistances represent the condition of membrane. Membrane dehydration level increases the ohmic resistance and which further results in the performance degradation. In the experiment, effects of cathode inlet relative humidity on low temperature PEMFC ( $65 \text{ }^\circ\text{C}$ ) durability during startup-shutdown cycling, Kim et al. reported that the ohmic resistance (approximately  $0.08 \Omega \text{ cm}^2$ ) of the single cells did not vary significantly with the cycle number and the cathode inlet relative humidity, implying that the membrane resistance was not substantially affected by the cathode inlet relative humidity during startup-shutdown cycling [13]. Unlike in the cell operation at low temperature, fully humidified condition, produced water in the system evaporates due to the high temperature in the HT-PEMFC operation under low humidified conditions; therefore, ohmic resistances respond to the inlet relative humidities sensitively in the HT-PEMFC operation. By using the commercial Nafion MEA, the reliability of GEIS was achieved.

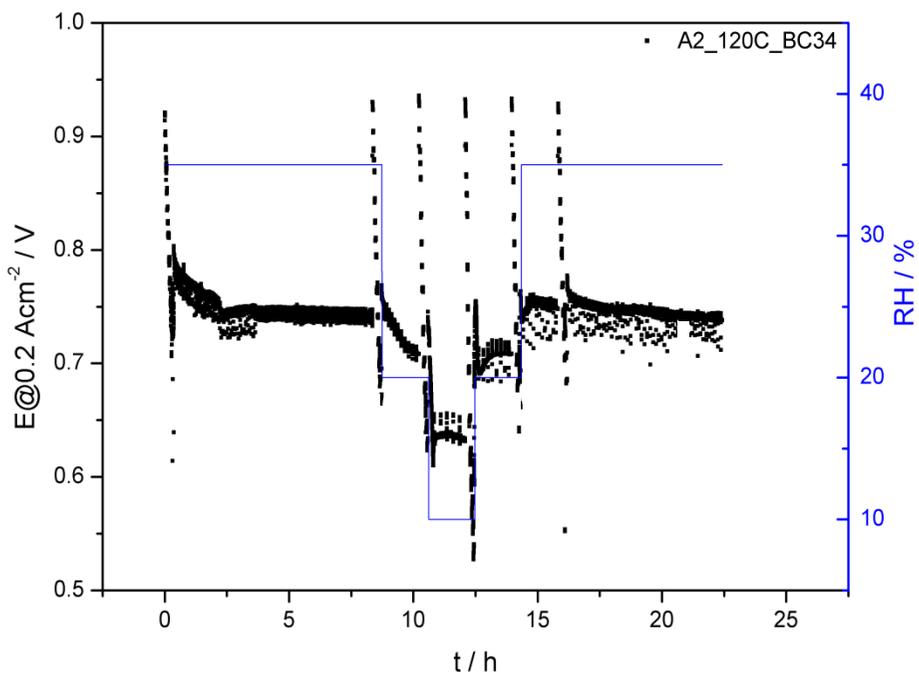


Fig. 11 Cell performance with varying RHs (10%, 20% and 35%).

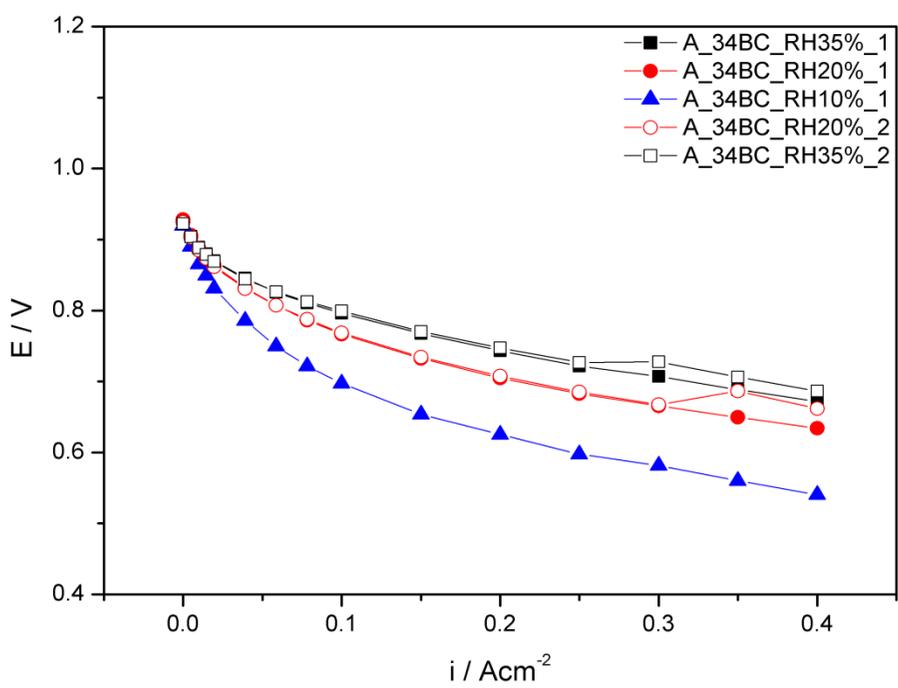


Fig.12 Polarization curves of Nafion MEA at RHs of 10%, 20% and 35%.

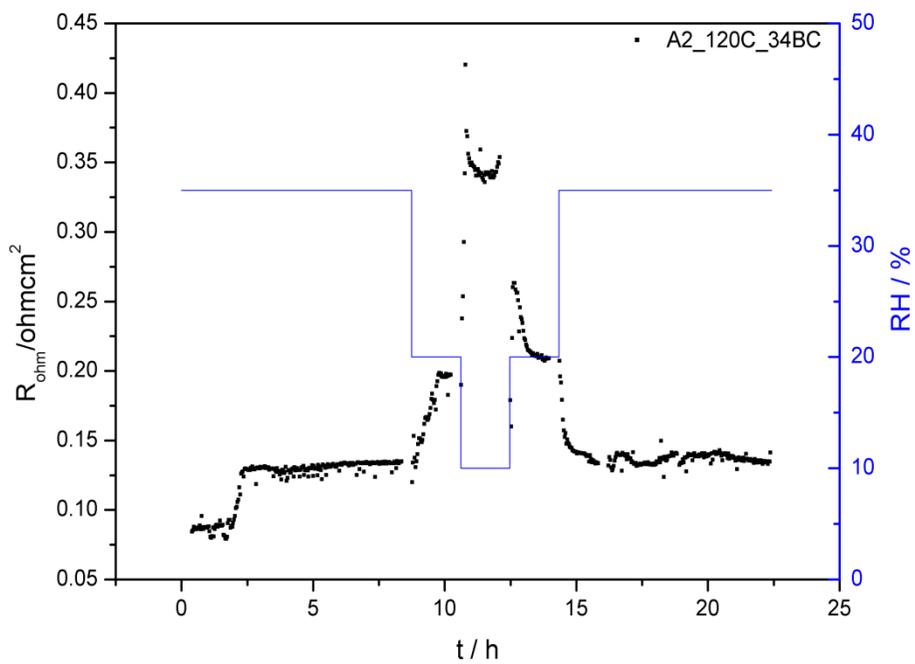


Fig. 13 Real-time ohmic resistances of Nafion MEA at RHs of 10%, 20% and 35%.

*Developed membrane, PES70\_S05* – The sulfonated poly(ether sulfone)-based silica nanocomposite membranes, PES70\_S05, has 70 mol% of hydrophilic moiety in the polymer backbone. It was synthesized via nucleophilic aromatic substitution polycondensation reaction. The chemical structure of the copolymer was characterized by NMR and FT-IR methods as reported in the paper written by Krishnan N.N [8]. Then, 5% (based on polymer) silica was added. The inorganic solid, SiO<sub>2</sub>, shows high water retaining capacity, therefore, it is believed that silica particles incorporated into proton conducting membranes would act as a water absorber and be able to provide sufficient proton conductivity by improving the membrane hydration at HT-PEMFC operation under low humidity [9].

To evaluate the PES70\_S05 through a single cell operation, an MEA has been produced with the developed membrane. As it was proven in the previous step that GDL 34 BC is more proper in the HT-PEMFC under low humidity application, GDL 34 BC was applied in this experiment. Then, the fuel cell was operated at constant current of 0.2 A cm<sup>-2</sup> with the operating condition at 120 °C, back pressure of 1.2 bars under low humidified condition. Due to the poor durability of PES70\_S05, monitoring the performance by varying the inlet relative humidities was not able to perform. During the cell operation, three i-V measurements were carried out at 0 h, 1 h and 2.5 h of the cell operation as shown in Fig. 14. Also, the cell performance at 0.2 A cm<sup>-2</sup> and ohmic resistances were collected in real-time by employing GEIS.

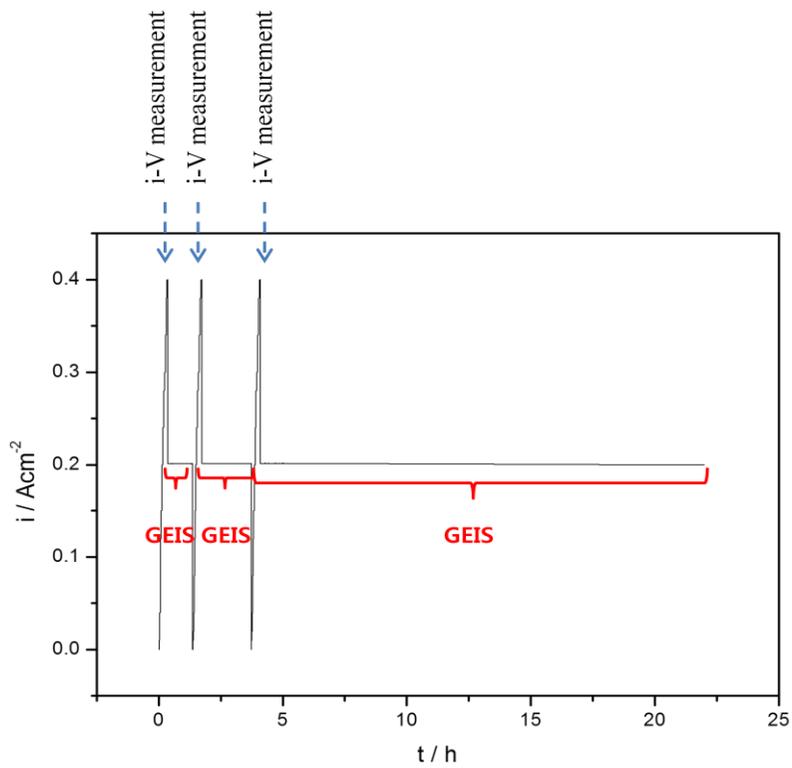


Fig. 14 Experimental profile for evaluation of PES7\_S05.

The single cell performance and durability at relative humidity of 35% was studied in Fig. 15. As shown in the figure, the rapid degradation of the cell performance was observed after 4 hours of the cell operation. The performances at 1 h, 3 h and 5 h of the cell were 0.740 V, 0.745 V and 0.455 V, respectively. Approximately 40% of the cell performance has been decreased in 4 hours. Poor chemical and mechanical stability of the PES70\_S05 membrane resulted in short life time of the cell. Fig. 16 shows polarization curves of PES70\_S05 MEA measured at 0 h, 1 h and 3.5 h of the HT-PEMFC under relative humidity of 35%. As the cell was operated, the performance was improved at 1 h. This phenomenon was also observed in the paper written by Silva et al. He concluded that the increase of the MEA performance along the activation procedure had the higher contribution due to the improvement of the catalyst activity. Also, the PEM played an important role on the increase of the triple phase boundary at the electrode/electrolyte interface [14]. After an hour of the cell operation, the cell performance of PES70\_S05 MEA was improved from 0.711 to 0.744 V (4% improvement) and the performance was close to the Nafion MEA performance at relative humidity of 35% which was determined as 0.743 V. Voltage jump was observed at the mass transfer region of the polarization curve. This phenomenon was explained by Song et al. He studied voltage jump during polarization of a PEM fuel cell when it was operated at low relative humidities. At zero current density, both the cathode and anode show the same values of moles of water per mole of sulfonic acid sites. As the current density increases the acid site gradient is created in the membrane. When the current density increases to a critical

value, the interface between the membrane and the anode catalyst layer becomes a liquid-equilibrated phase, resulting in a rapid improvement of anode reaction kinetics. This improvement causes a voltage jump in the polarization curves [15].

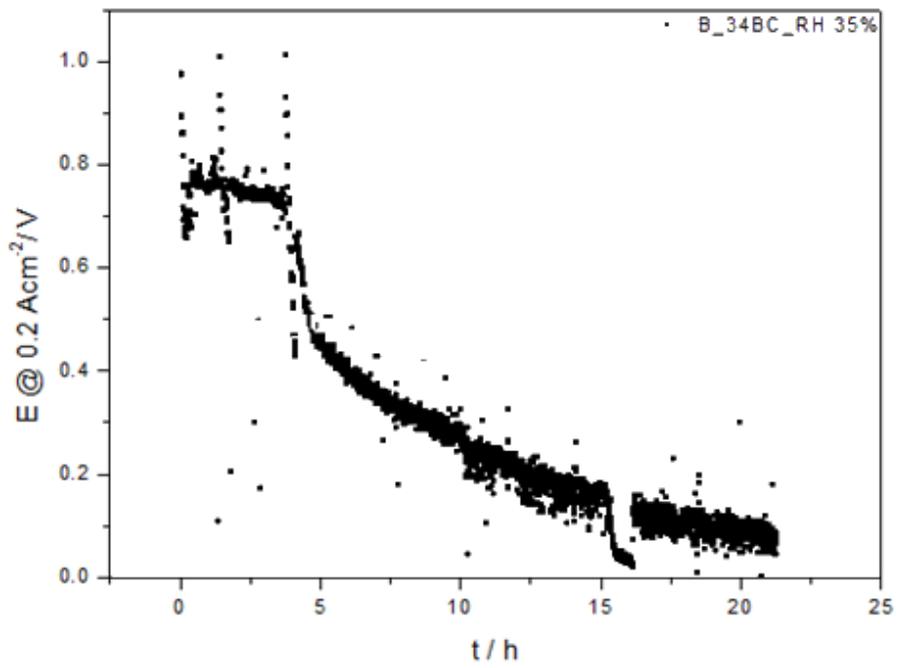


Fig. 15 Performance of PES70\_S05 MEA at 120 °C, RH of 35%.

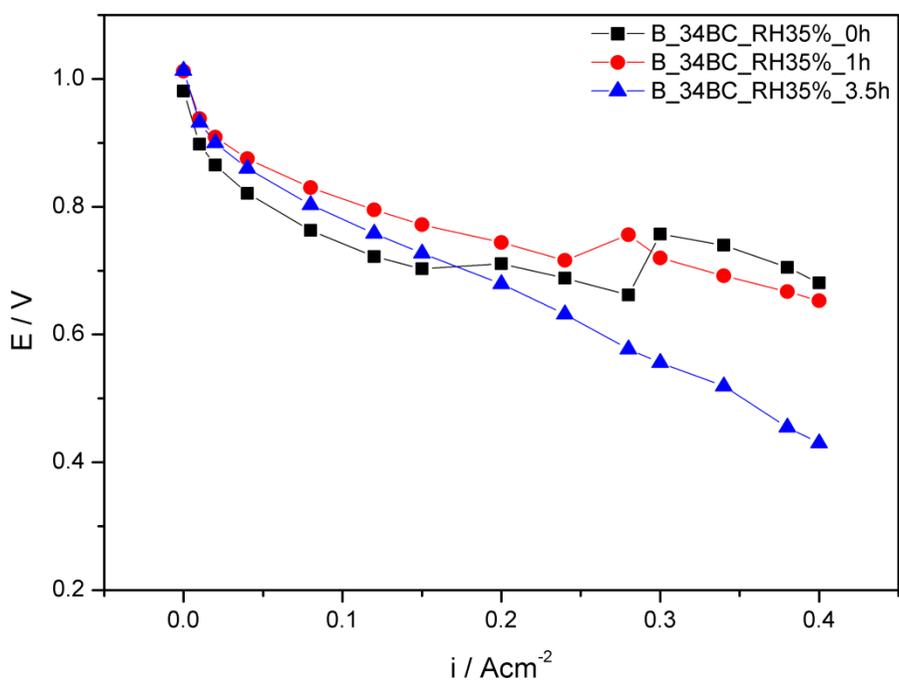


Fig. 16 Polarization curves of PES70\_S05 MEA at 0 h, 1 h and 3.5 h.

By applying GEIS at 0.2 A cm<sup>-2</sup>, 1 kHz, real-time ohmic resistances were collected as shown in Fig. 17. From the plot, rapid increase in ohmic resistance after 3.5 hours of the cell operation was observed. Between 2 and 5 hours of the cell operation, the ohmic resistance was increased from 0.444 Ω cm<sup>2</sup> to 1.80 Ω cm<sup>2</sup> which was increased by four times in three hours. This implies that PES70\_S05 has been degraded due to dehydration at high temperature even though the glass transition temperature (235 °C) is higher than the cell operating temperature. With the ohmic resistance taken during the cell operation, its proton conductivity was calculated using the following equation:

$$\sigma\left[\frac{S}{cm}\right] = \frac{l[cm]}{R_{ohm}[\Omega] \times A[cm^2]}$$

where  $\delta$  is the proton conductivity (through plane),  $l$  is the distance between the two potential probes, which is the membrane thickness in this case ( $22 \times 10^{-4}$  cm),  $R_{ohm}$  is the resistance of the membrane from the impedance spectra, and  $A$  is the cross sectional area, which is the electrode area ( $10.24$  cm<sup>2</sup>) in this application.

The calculated proton conductivity was plotted as in Fig. 18. As the high temperature cell operation under low humidity carried on, proton conductivity was reduced to quarter, which was 4.95 mS cm<sup>-1</sup> to 1.22 mS cm<sup>-1</sup>, within three hours. Finally, reduction of the conductivity led to the performance degradation. To study the relationship between the membrane degradation and performance degradation, the absolute values of performance reduction and  $iR$  drop compared to the initial performance were plotted with time in Fig. 19.

By plotting them together, it was clearly showed that iR drop was the main factor of the performance decay. 88% of performance reduction occurred between 2 hours and 5 hours was caused by iR drop. Therefore, the development of the membrane with chemical and electrochemical stability at high temperature under low humidified condition while satisfying high proton conductivity is crucial. Lastly, the proton conductivity during the cell operation (in-situ) and proton conductivity obtained using a four-probe-conductivity (ex-situ) were compared. The in-plane proton conductivity of each membranes was measured using a four-probe-conductivity cell in the temperature and humidity controlled chamber. Fig 20 represents the proton conductivity at different relative humidity of inlet gas. The figure shows that the conductivity obtained using in-situ technique is much higher than that using ex-situ. When the relative humidity of 35% was applied at 120 °C, the ex-situ membrane proton conductivity was  $0.247 \text{ mS cm}^{-1}$ , however, the in-situ proton conductivity was  $4.95 \text{ mS cm}^{-1}$  which has been increased by 20 times. This conductivity was the same as the ex-situ conductivity at relative humidity of 63%. In other words, water produced during the cell operation enhanced proton conductivity by improving membrane hydration. Thus, the in-situ technique is necessary to study the actual behavior of the membrane during the cell operation.

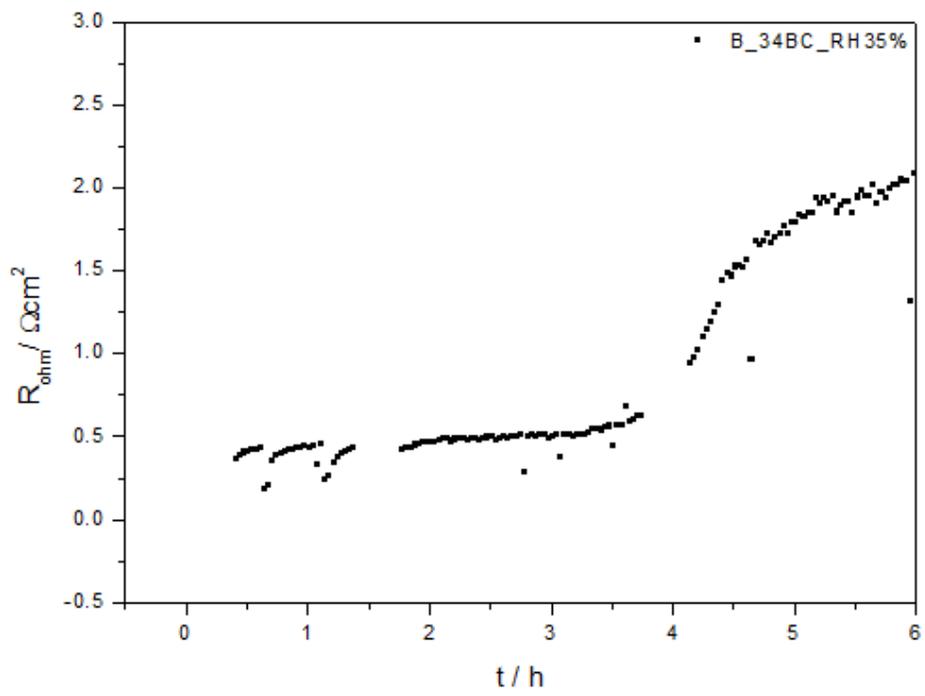


Fig. 17 Real-time ohmic resistances of PES70\_S05 MEA at RH of 35 %.

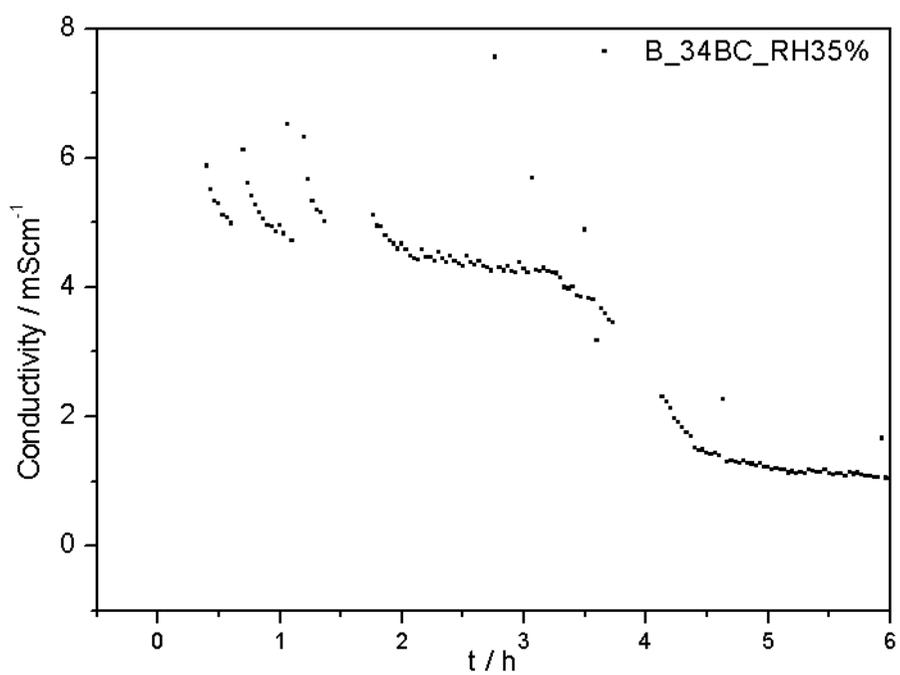


Fig. 18 Proton conductivity of PES70\_S05.

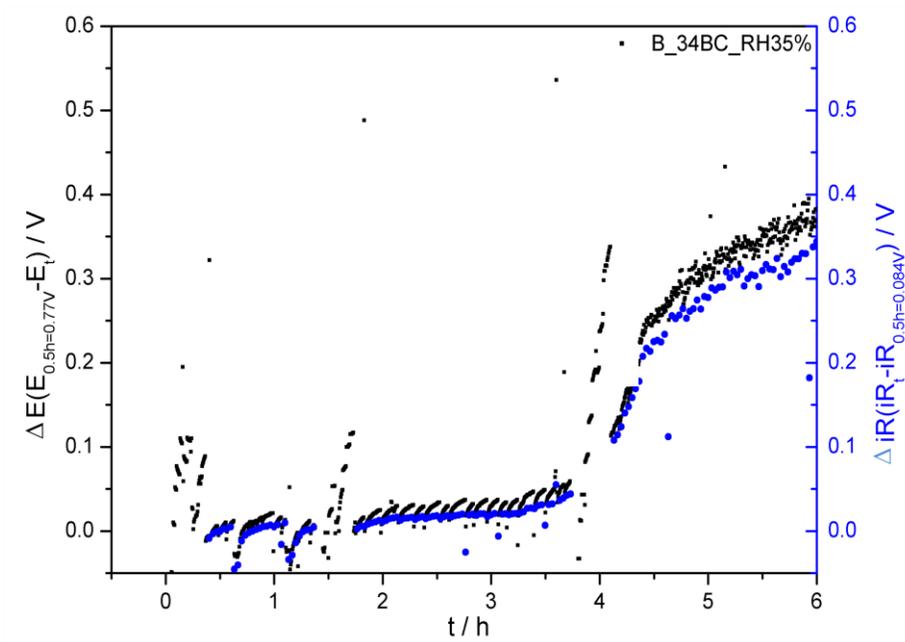


Fig. 19 Comparison of  $\Delta E$  and  $\Delta iR$  drop of PES70\_S05 MEA.

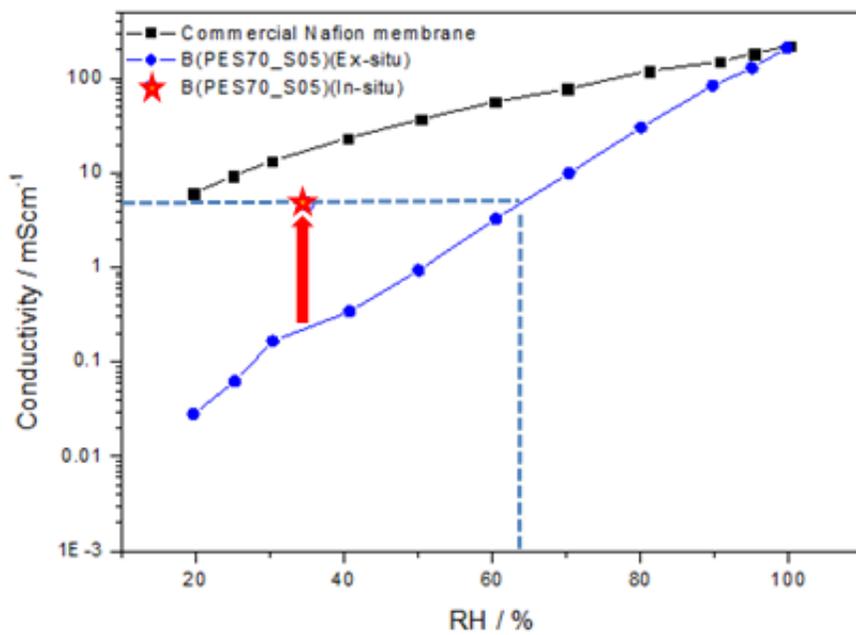


Fig. 20 Proton conductivity of Nafion membrane and PES70\_S05 with RHs.

## 4. Conclusion

In this work, optimization of operating conditions such as applying different porosity of GDL with back pressure was performed to enhance the performance of HT-PEMC operation under low humidity. PEMFCs operated at high temperature (120 °C) under low humidified conditions (RHs of 10%, 20% and 35%) were studied to investigate the characteristics of HT-PEMFC via electrochemical techniques established and designed to monitor developed membranes effectively. The experimental results showed that operating HT-PEMFC by applying lower porosity of GDL brought a significantly improved performance and durability by reducing the water evaporation rate. Through employing the in-situ technique, galvanostatic electrochemical impedance spectroscopy (GEIS), analysis of the membrane behavior during the cell operation was accomplished. Through this technique, it was observed that produced water during the cell operation enhances the proton conductivity of the membrane and performance. Also the dependence of MEA performance on the relative humidities was studied. Therefore, maintaining the hydration inside the system is needed by developing membrane and possible to improve the hydration by adjusting the cell operating condition for HT-PEMFC applications.

## References

- [1] J. Andrews and B. Shabani, "Re-envisioning the role of hydrogen in a sustainable energy economy," *International Journal of Hydrogen Energy*, vol. 37, pp. 1184-1203, 2012.
- [2] C.-J. Winter, "Hydrogen energy — Abundant, efficient, clean: A debate over the energy-system-of-change," *International Journal of Hydrogen Energy*, vol. 34, pp. S1-S52, 2009.
- [3] Y. Wang, K. S. Chen, J. Mishler, S. C. Cho, and X. C. Adroher, "A review of polymer electrolyte membrane fuel cells: Technology, applications, and needs on fundamental research," *Applied Energy*, vol. 88, pp. 981-1007, 2011.
- [4] W. R. Grove, "On a Gaseous Voltaic Battery," *Philosophical Magazine and Journal of Science*, vol. XXI, pp. pp 417-420, 1842.
- [5] R. P. O'Hayre, Cha, S.W., Colella, W., Prinz, F.B., *FUEL CELL FUNDAMENTALS*. New York: John Wiley & Sons, 2006.
- [6] J. Zhang, Z. Xie, J. Zhang, Y. Tang, C. Song, T. Navessin, Z. Shi, D. Song, H. Wang, D. P. Wilkinson, Z.-S. Liu, and S. Holdcroft, "High temperature PEM fuel cells," *Journal of Power Sources*, vol. 160, pp. 872-891, 2006.
- [7] S. Bose, T. Kuila, T. X. H. Nguyen, N. H. Kim, K.-t. Lau, and J. H. Lee, "Polymer membranes for high temperature proton exchange membrane fuel cell: Recent advances and challenges," *Progress in Polymer Science*, vol. 36, pp. 813-843, 2011.
- [8] N. N. Krishnan, H.-J. Lee, H.-J. Kim, J.-Y. Kim, I. Hwang, J. H. Jang, E. A. Cho, S.-K. Kim, D. Henkensmeier, S.-A. Hong, and T.-H. Lim, "Sulfonated poly(ether sulfone)/sulfonated polybenzimidazole blend membrane for fuel cell applications," *European Polymer Journal*, vol. 46, pp. 1633-1641, 2010.
- [9] N. N. Krishnan, D. Henkensmeier, J. H. Jang, H.-J. Kim, V. Rebbin, I.-H. Oh, S.-A. Hong, S.-W. Nam, and T.-H. Lim, "Sulfonated poly(ether sulfone)-based silica nanocomposite membranes for high temperature polymer electrolyte fuel cell applications," *International Journal of Hydrogen Energy*, vol. 36, pp. 7152-7161, 2011.
- [10] S. Shimpalee, U. Beuscher, and J. W. Van Zee, "Analysis of GDL flooding effects on PEMFC performance," *Electrochimica Acta*, vol. 52, pp. 6748-6754, 2007.

- [11] B. Wahdame, D. Candusso, F. Harel, X. François, M.-C. Péra, D. Hissel, and J.-M. Kauffmann, "Analysis of a PEMFC durability test under low humidity conditions and stack behaviour modelling using experimental design techniques," *Journal of Power Sources*, vol. 182, pp. 429-440, 2008.
- [12] P. Choi, "Thermodynamics and Proton Transport in Nafion II. Proton Diffusion Mechanisms and Conductivity," *Journal of The Electrochemical Society*, vol. 152, pp. E123-E130, 2005.
- [13] 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," *Journal of The Electrochemical Society*, vol. 157, p. B104, 2010.
- [14] V. B. Silva and A. Rouboa, "Hydrogen-fed PEMFC: Overvoltage analysis during an activation procedure," *Journal of Electroanalytical Chemistry*, vol. 671, pp. 58-66, 2012.
- [15] C. Song, C. Jensen Chua, Y. Tang, J. Zhang, J. Zhang, J. Li, K. Wang, S. McDermid, and P. Kozak, "Voltage jump during polarization of a PEM fuel cell operated at low relative humidities," *International Journal of Hydrogen Energy*, vol. 33, pp. 2802-2807, 2008.
- [16] S. Shimpalee, U. Beuscher, J.W. Van Zee, "Analysis of GDL flooding effects on PEMFC performance," *Electrochimica Acta*, vol. 52, pp. 6748-6754, 2007.
- [17] C. Chung, L. Kim, Y. Sung, J. Lee, J. Chung, "Degradation mechanism of electrocatalyst during long-term operation of PEMFC." *International Journal of Hydrogen Energy*, vol. 34, pp. 8974-8981, 2009.
- [18] Z.B. Wang, P. Zuo, Y. Chu, Y. Shao, G. Yin, "Durability studies on performance degradation of Pt/C catalysts of proton exchange membrane fuel cell." *International Journal of Hydrogen Energy*, vol. 34, pp. 4387-4394, 2009.
- [19] C. Chen, T.F. Fuller, "The effect of humidity on the degradation of Nafion® membrane." *Polymer Degradation and Stability*, vol. 94, pp. 1436-1447, 2009.
- [20] S. Kim, I. Hong, "Effects of humidity and temperature on a proton exchange membrane fuel cell (PEMFC) stack." *Journal of Industrial and Engineering Chemistry*, vol.14, pp. 357-364, 2007.
- [22] Y. Nagahara, S. Sugawara, K. Shinohara, "The impact of air contaminants on PEMFC performance and durability." *Journal of Power Source* , vol.

- 182, pp: 422-428, 2008.
- [23] A. C. Fernandes, E. A. Ticianelli, "A performance and degradation study of Nafion 212 membrane for proton exchange membrane fuel cells." *Journal of Power Sources*, vol. 193, pp. 547-554, 2009.
- [24] T. V. Reshetenko, G Bender, K. Bethune, R. Rocheleau, "Systematic study of back pressure and anode stoichiometry effects on spatial PEMFC performance distribution." *Electrochimica Acta* , vol. 56, pp: 8700-8710, 2011.

# 초 록

## 고온 저가습에서의 고분자 전해질 막 연료전지 단위전지의 운전 특성 연구

조민경

공과대학 화학생물공학부

서울대학교 대학원

고온 (120 °C) 저 가습 고분자 전해질 막 연료전지는 화학적 전기화학적 안전성을 보완하면서 성능과 내구성의 향상에 어려움이 있다. 본 연구에서는, 아직 초기 단계에 있는 고온 연료전지 연구를 위하여 연료전지 운전 조건을 고온 저 가습 운전에 알맞게 개선 한 후 특성분석 방법 확립 및 연구를 진행하였다. 투과성이 낮은 공기 확산 층을 이용하여 막-전극 접합체의 단위 전지 성능을 평가 하였다. 이때, 40 시간 동안의 성능 저하는 12.0 % 에서 2.78% 로 줄어들었음을 확인하였고, 60 시간에서 100 시간이상으로 약 2 배 정도의 내구성이 향상되었다. 또한, 고 주파를 이용한 정전류 임피던스 방법을 도입하여 상대습도 에 따른 실시간 막 전극 저항의 변화 연구를 가능하게 하였다. 이 실험을 통하여, 다음과

같은 결과를 얻어 내었다. 전지운전을 통하여 생성된 물은 연료전지 내에서의 이온전도도를 완화하여 성능을 향상시켰다. 막 저항의 경우, 상대습도와 반비례 하는 성향을 보였으며 (저습 상태에서는 막 저항이 높아짐) 막마름 현상으로 인한 막의 열화가 성능 저하의 주요 원인으로 작용 하였다.

주요어 : 고온, 고분자전해질막 연료전지, 기체확산층, 이온전도도, 저가습

학 번 : 2010-24103