CHAPTER 1 INTRODUCTION

1.1. Rational/Problem Statement

The power generation from a "Fuel cell" is electricity produced from electrochemical reactions. With no pollution, all types of fuel cells are classified as clean energy systems since the product of a fuel cell reaction is water. Not only is a fuel cell system as noiseless as a solar cell system but also it can provide stable electricity more than the power from a solar cell and also a wind turbine.

For a typical low temperature fuel cell such as a proton exchange membrane fuel cell (PEMFC), hydrogen is the main fuel and oxygen is the main oxidant at the anode and the cathode, respectively. However, some other types of fuel cells can be fed by alcohol (such methanol or ethanol) or natural gas (such methane) at the anode side, but cell's performance is lower than a hydrogen fuel cell. Also, air is selected as a feed at the cathode side since it is abundantly available and much cheaper than pure oxygen.

Alcohol fuel cells or liquid fuel cells have an advantage of mobility because liquid fuels are easily carried without needing high pressure or a safety cylinder to store the fuel. The development of an electricity power source as a portable power supply unit from alcohol fuel cells has been highly attractive with this advantage of liquid fuels.

Direct methanol fuel cells (DMFCs) can be used as portable units for small-scale applications, such as laptop computers and mobile phones, due to their good energy efficiency, ease of operation at ambient pressure, high power density, and the simplicity of system structure [1-4].

However, for practical operation of portable power units, such as DMFCs in reality, the load profile of the devices changes according to their working capacity. Furthermore the load is turned on and off frequently depending on the user's habits. In addition, stable operation of a DMFC requires more than one thousand hours, which can be difficult to achieve, due to its drawbacks such as electrocatalyst dissolution, membrane degradation and other problems resulting from methanol crossover. Such types of operation may induce accelerated degradation of cell performance.

This research work on the DMFC's performance degradation has focused on the causes from cycling operation. Fading behavior of MEA and cause of cell performance degradation were investigated under different patterns of cycling operation. For the first part, the set-up of methanol-O_2 system was carried out, while in the second part, methanol-air system was performed. In both systems, the effect of cycling operation on the performance degradation was investigated as well as the cause of degradation, but the details in cycling operation and the MEA used in both systems were different. In addition, the effect of thermal cycling was added to prove the Pt catalyst particle agglomeration with different level of temperature under cycling of time period.

To investigate the fading behavior of the DMFC, which consist of a PtRu catalyst for anode and a Pt catalyst for cathode under the cycling operation was simulated from a real working condition of portable electrical devices in an attempt to understand the causes of DMFC degradation and its severity on the cell's performance. A comparison with the system tested in a continuous operation was performed by using cell polarization, frequency response analysis (FRA) and cyclic voltammogram (CV) as in-situ techniques. Moreover, ex-situ techniques, such as transmission electron microscopy (TEM), X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDX) were used to identify the physical change of electrode before and after the stability test on the effect of cycling operation.

Moreover, from the cycling operation of DMFC previously studied, the thermal cycling effect was investigated on the change of the size diameter and size distribution of the Pt electrode catalyst particle under different thermal cycling time. The metal catalyst size changed was explored by using ex situ measurements of TEM and XRD to determine the reduction of catalyst surface area that influences the loss of cell activation to accelerated cell performance decay.

1.2. Literature Review

There are many factors which are believed to be responsible for the loss of stability of the membrane electrode assembly (MEA) in DMFCs, which include methanol crossover [5], and catalyst agglomeration [6] that causes the loss of catalytic active area [7], and catalyst poisoning due to accumulated intermediates or impurities on the catalyst [8], and also deterioration of the polymer electrolyte membrane [9]. In addition, the presence of liquids can accelerate the sintering process of catalyst particles [10], and methanol solution is aggressive to the Nafion® polymer electrolyte [11] as swelling membrane so it leads to peeling and cracking in the contact boundary [12]. In order to understand some of the above said issues, it is necessary to study the degradation of DMFCs especially under a long-term operation.

The DMFC degradation study was carried out with normal operation under a constant load profile by a few research groups. In 2003, the group of Jianguo et al. [7] found that 30% of the original maximum power density of a DMFC was lost after a 75 h life test at a low current density of 100 mA cm^{-2}. The rate of power density loss at -0.32 mW cm^{-2} hr^{-1} was observed. The decrease of cell power density was caused by the electrode cracking from the membrane due to the different degrees of swelling of the electrode and membrane, and also, the agglomeration of electrocatalysts in the anode that create bigger particle sizes than in the cathode since methanol might be more aggressive towards electrocatalysts than is water. After that for 3 years, in 2006, the group of Jeon et al. [13] reported that DMFC (PtRu black anode) performance degradation depended on the different current densities of operations during 145 hrs. At high current densities of 200 mA cm^{-2}, the power density loss was from 78 mW cm^{-2} to 35 mW cm^{-2} or -0.296 mW cm^{-2} hr^{-1}. But, at 100 mA cm^{-2}, the cell power density was reduced to 65 mW cm^{-2} (from initial 70 $mWcm^{-2}$) or -0.034 mW cm^{-2} hr^{-1}. The performance loss at high current density was caused by the catalyst agglomeration and dissolution of Ru with the formation of formic acid as a by-product of methanol oxidation.

During the year of 2006, the performance loss during longer running hours of DMFCs was investigated, by the group of Weimin et al. [12]. A 500 h operation on a DMFC under a constant current at 70 mA cm^{-2} was carried out. The results revealed that the particle size of electrocatalysts increased with test time and the rate of sintering was faster in cathode than in anode which contrasts with Jianguo et al.'s results because the existence of ruthenium oxides or hydroxide in anode catalyst can inhibit the agglomeration of catalyst crystallites. Also, the increase of particle size and the poison of electrocatalysts by intermediates and impurities gave a higher loss of electro chemical area (ECA) ratio than that ratio of specific surface area (SSA) loss. Furthermore, after life-test, some ruthenium penetrated through the membrane from the anode side to the cathode side was indicated as the phenomenon of Ru crossover. In addition, Ho et al. [16] reported that a resistance to mass transport was identified due to the decrease of the GDL contact angle which is a morphology alteration and redistribution of the fluorinated water proofing agent in the GDLs and MPLs on cathode side after 1,000 h operation.

Furthermore, the changes of microstructure, surface composition, the interfacial structure of the MEA, and the aging of Nafion® under the DMFC lifetime tests were also observed by Xuan et al. [9]. The results revealed that there was significant performance degradation during the first 200 h operation; while the degradation was slowing down between 200 and 704 h operation and, finally, the degradation became worse after 1002 h operation. After test time, it was found that the mean particle sizes of both anode and cathode catalysts became larger. Also, At the anode, the metal oxide species was identified from the PtRu black surface. Moreover, the increase in the crystallinity of membrane was also observed after the single cell lifetime test.

After 2006, the period of test time on DMFC operation under constant drawing current density was extended. At 2,000 h, the DMFC operation was conducted by Junsong et al. [14]. The anode catalyst of polyol-synthesized PtRu/C was used to fabricate MEA for DMFC. The decay of cell voltage, at constant current mode of 100 mA cm^{-2}, was 0.33 V from initial at 0.48 V and the rate of power density loss during test time was -0.0075 mW cm^{-2} hr^{-1}. In anode, Ru leaching is the main reason for cell degradation because the stability of PtRu/C closely depends on the anode potential. Under an anode potential less than 0.363V versus DHE, there exists a stable discharging period. When the anode potential exceeds 0.363V versus DHE, the performance of the anode degrades dramatically due to the leaching of unalloyed Ru and then the proton-conducting hydrous ruthenium oxides (RuO_xH_y) adds another mechanism for the increase of internal resistance. Furthermore, the nano-particles of Pt were unstable with high aggregation and ripening under the cathode working potential in the range of 0.8-1.0V versus DHE, leading to the drop of ESA and oxygen reduction potential. Moreover, Weimin et al. [12] tested the anode catalyst of 30 wt % Pt–15 wt% Ru/CNT. The results showed a slower fall in cell voltage performance from 0.44 V to 0.37 V at constant drawing current density of 70 mA cm^{-2} during 500 hrs and the power density rate was -0.0098 mW cm^{-2} hr^{-1}. The additional cause of cell performance degradation from previous was a Nafion® dissolution and Ru crossover from anode to cathode. Also, the effect of methanol feed on the anode dissolution and swelling of membrane was concerned.

Since the operation of direct methanol fuel cell (DMFC) may cause several disadvantages, such complex causes of DMFC degradation, the summary diagram and following explanation of DMFC degradation with complex causes from the long term operation are shown in Figure 1.1.

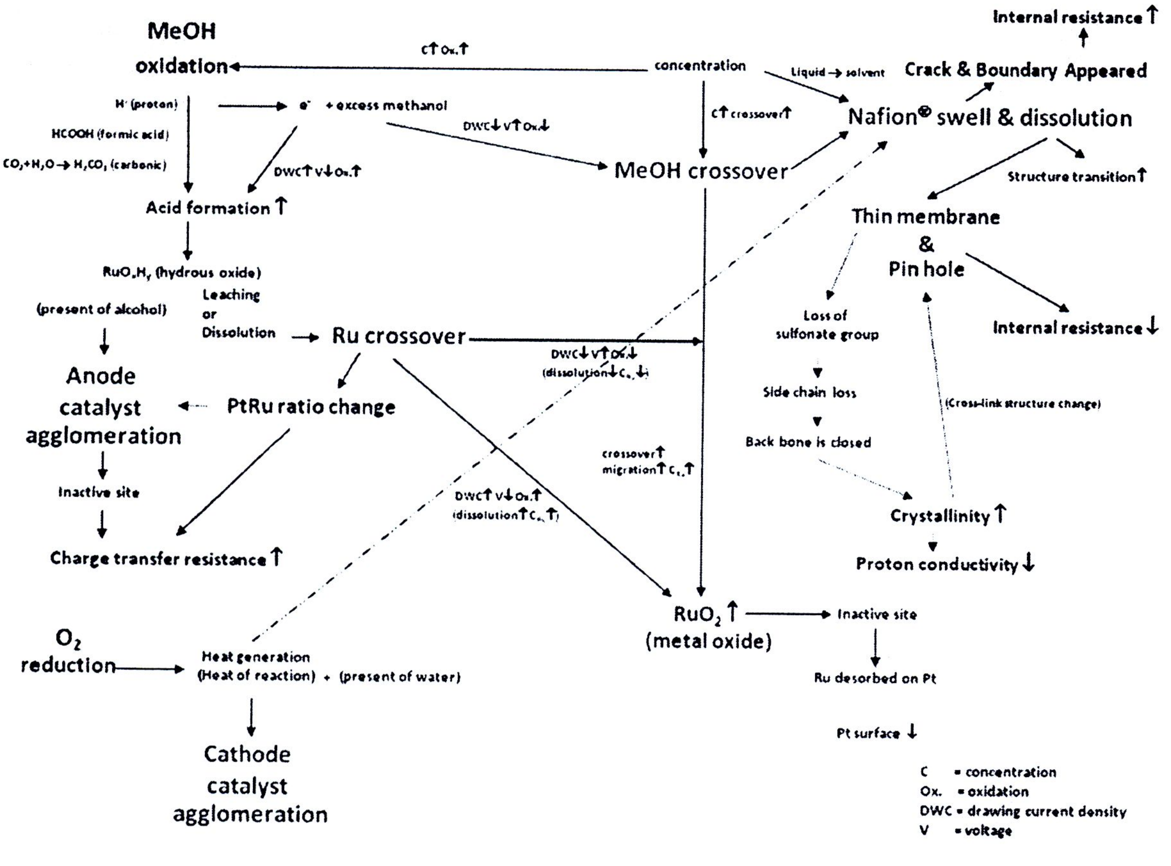

Figure 1.1 The complex causes of DMFC degradation diagram.

Starting with methanol oxidation on the PtRu catalyst surface, the acid environment is formed from by product as proton (H^+) and formic acid (HCOOH). This acid condition affect to the hydrous oxide of Ru (RuO_xH_y) then cause the leaching or dissolution of un-alloy Ru. After that, this metal Ru is moved through the membrane of Nafion® which is swelled by pore extended under the environment of alcohol as methanol to the cathode side and then the occupation of RuO_2 formation on the surface of the electrode is served. The loss of un-alloy Ru at anode side and RuO_2 formation at cathode side give the reduction of the reaction area on both side of electrode catalyst.

Also, loss of active sites as catalyst agglomeration can occur on both sides under two conditions for cell operation at high drawing current density and at open circuit voltage (OCV). For anode side, when the electron is generated under condition of high current, the heat which from the moving of electron and the exothermic reaction plus the external system heat provided can cause the agglomeration of catalyst particle. At the cathode, the particle of catalyst can be formed a big size of particle when the cell operated at OCV. This OCV condition serves more fuel crossover of methanol from anode to cathode and then the methanol can react directly with oxygen on Pt catalyst surface as a direct combustion of methanol. This combustion provides more heat gain on metal catalyst region, then the particle agglomeration occurs.

The Ru dissolution at anode side, RuO_2 formation at cathode side and the catalyst agglomeration on both sides of fuel cell electrode cause a metal catalyst surface loss. This loss reduces the activation performance and the region of activation loss in the performance curve may drop dramatically.

Furthermore, the methanol crossover causes the reduction of an OCV value and the swelling of Nafion® membrane. In cases of the OCV value, this fuel crossover gives a current flow through the membrane as an internal current and then the value of OCV drops. Furthermore, a strongly polar liquid such as methanol solution inside the Nafion® membrane serves to extend pore size as swelling of membrane and some of side chain of membrane is detach out called Nafion® dissolution. This dissolution make a thinner membrane since when the side chain is lost, the back bone is closed. Therefore, at high frequency, the internal resistance of cell impedance is low but the proton conductivity is high due to the formation of membrane crystallinity during long term of the methanol crossover.

Moreover, the swelling of Nafion® content in catalyst layer and membrane causes peeling and cracking in the catalyst layer. The peeling and cracking affect the internal resistance for electron and proton transfer. This increase value affects the ohmic loss and the overall cell performance is reduced.

To investigate the degradation of cell components during long-term operation, a constant load was applied to the cell but with different test times from 75 hr [7] until 2,020 h [14]. A few researchers focused on the variable load conditions but for investigating the dynamic response of output current and voltage response for vehicle application [15]. No other previous work has reported combining a variable load profile and long term operation to investigate cell performance loss with respect to anode activity during test time. Therefore, long-term operation with varied load is more challenging and still needs to be explored for a successful application of DMFCs in next generation power sources.

1.3. Research Objectives

In this study, a cycling operation was conducted to evaluate the effects of direct methanol fuel cell (DMFC) operating conditions on the degradation of electrode and membrane electrode assembly (MEA). The loss of DMFC performance during cycling operation was investigated by using in-situ and ex-situ techniques. The fading behavior of DMFC during test time was carried out following the 2 main objectives:

- To study the effect of cycling operation on the DMFC performance loss of methanol-O_2 feed and methanol-air feed.
- To determine the cause of DMFC degradation under cycling operation.

The scope of work

The life-tests of DMFCs were carried out for two systems with methanol-O_2 feed and methanol-air feed. The cycling operational was set as start-run-stop (SRS) for 5 days with respect to long-running (LR) modes at methanol-O_2 system and the step-cycling-operation (SCO) respect to long-running for 100 h (LR-100) at methanol-air system. For the sample of membrane electrode assembly, the anode used PtRu/C catalyst type, while, Pt/C was employed for the cathode. Also, a Nafion® membrane was used for the solid polymer electrolyte.

Both in-situ and ex-situ measuring methods were employed to evaluate the fading behavior during test time. The identification methods for investigating degradation causes under cycling operation were performed by the following techniques:

- *In-situ technique*

(1) Linear sweep voltammogram was used for determining the metal surface loss of metal catalyst such as the catalyst agglomeration by measuring the change of anode potential, and the ruthenium dissolution by exploring the onset potential

(2) Cyclic voltammogram was performed for measuring the shift of oxidation peak potential to explore the loss of Ru. Also, the reduction of oxidation peak can represent a problem on the catalyst surface.

(3) Frequency response analysis was applied for evaluating the fading of cell (or anode) internal resistance, charge transfer resistance, morphological properties of the electrode, chemical double layer of the electrode, and absorption phenomena or diffusion effect, and electro-oxidation reaction resistance of adsorbed species.

(4) Polarization was recorded for measuring the value of open circuit voltage that could represent the occurrence of methanol crossover. Also, the curve could give the loss of catalyst activation, cell ohmic resistance, and mass transport.

- *Ex-situ technique*

(1) TEM image could represent the size and size distribution of catalyst particles as the catalyst agglomeration.

(2) XRD pattern was employed to explore the change of metal phase with peak position or peak intensity reduction. This result could imply the loss of Ru or particle size change.

(3) EDX data could give the result or the change of PtRu bimetallic ratio that is related to the Ru dissolution after applying the cycling operation.