CHAPTER 3 METHODOLOGY

The two main objectives of this research are to focus on the cell performance degradation and the cause of fading behavior of DMFC electrode and electrolyte under cycling operation. For the first part, the set-up was carried out in a methanol-O_2 system, while the second part was in a methanol-air system. In both systems, the effect of cycling operation on the performance degradation was investigated as well as the cause of degradation, but the details of the cycling operation and the MEA used in both systems were different.

3.1 System operation

In this section, each system operation of fuel and oxidant feed was applied to the different patterns of the cycling operation to the 5 cm^2 membrane electrode assembly (MEA), which consists of PtRu/C at anode and Pt/C at cathode, and Nafion® membrane as a solid electrolyte. The DMFC performance test under different operating modes was measured.

3.1.1 Methanol-O_2 system

For the first part, in the methanol-O_2 system, the cell was operated under start-run-stop mode and long-run mode for 5 days, designated as SRS and LR, respectively. For the SRS mode, the cell was manipulated for three consecutive cycles before it was left overnight in de-ionized water. Each cycle consisted of two periods: running and stopping periods. The diagram of the cell operational modes is shown in Figure 3.1. During the running period, the cell was operated with a methanol solution feed at the anode and O_2 at the cathode. It was regulated at 80 °C and 2×10^5 Pa, and discharged in a potentiostatic mode with a constant voltage of 0.3 V, whereas in the stopping period, the cell was still exposed to the methanol solution at room temperature and atmospheric pressure under the open circuit voltage (OCV). For each day of the LR mode, the cell was operated continuously for 15 h under the same condition as the running period in the SRS mode and then it was rested in de-ionized water. The 15 h for DMFC operation per day and 5 days per week, this condition was similar to the behavior of users who operate portable devices, such as laptop computers, in their daily lives.

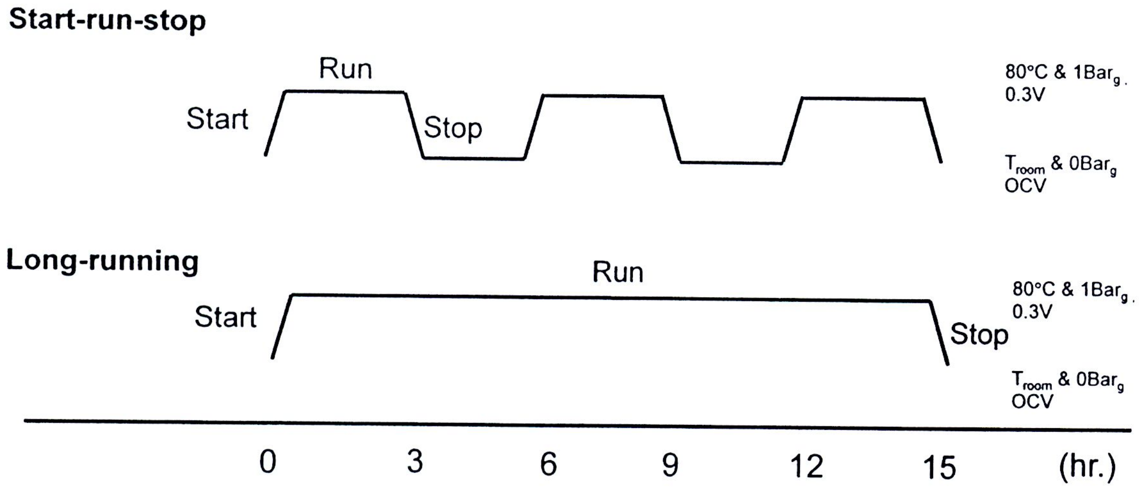


Figure 3.1 Diagram of operational mode per day of SRS and LR.

In the part of SRS and LR modes, the active area of the MEAs made was 5 cm^2. The 20 wt.% PtRu/C (C13–20 HP Pt:Ru alloy (1:1 a/o) on Vulcan XC72, E-TEK) catalyst ink was prepared at catalyst loading of 1.5 mg cm^{-2} with de-ionized water, isopropyl alcohol and a Nafion® ionomer solution as the anode catalyst. The catalyst ink was repeatedly sonicated to ensure homogeneous mixing and then applied to the gas diffusion layer by painting. The gas diffusion layer was made by spraying the mixture of Vulcan XC72 and PTFE in isopropanol on a carbon cloth (ETEK) which was then baked at 330 °C for 1 h. The finished anode was heated at 110 °C for 1 h. The commercial gas diffusion electrode (E-LAT®, E-TEK) containing 0.5 mg cm^{-2} of Pt on Vulcan XC72 was used as an oxygen electrode. The MEA was fabricated by positioning the anode and cathode on both sides of a pretreated Nafion®115 membrane and hot-pressing for 90 s at 150 °C and 300 psi. The single cell was then obtained by sandwiching both sides of the MEA with a graphite plate of a commercial housing (Electrochem. Inc.). The cell was activated under a hydrogen flow for 24 h before a life-test. The schematic diagram of the test station and in situ analysis equipment for the life-test of DMFC is shown in Figure 3.2. During the life-test, the single cell was tested by feeding a methanol solution (1 mol L^{-1}) and oxygen into the anode and cathode at a flow rate of 1 mL min^{-1} and 180 mL min^{-1} (2 × 10^5 Pa), respectively, at the condition described above. The decaying of cell polarization was collected during test time.

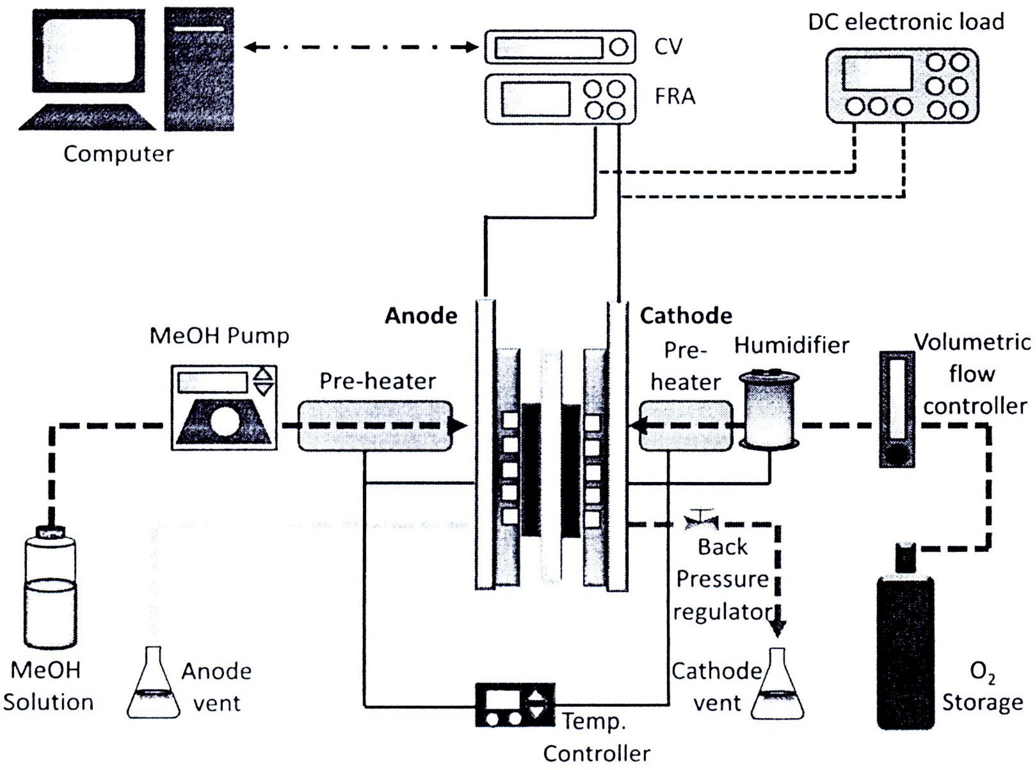
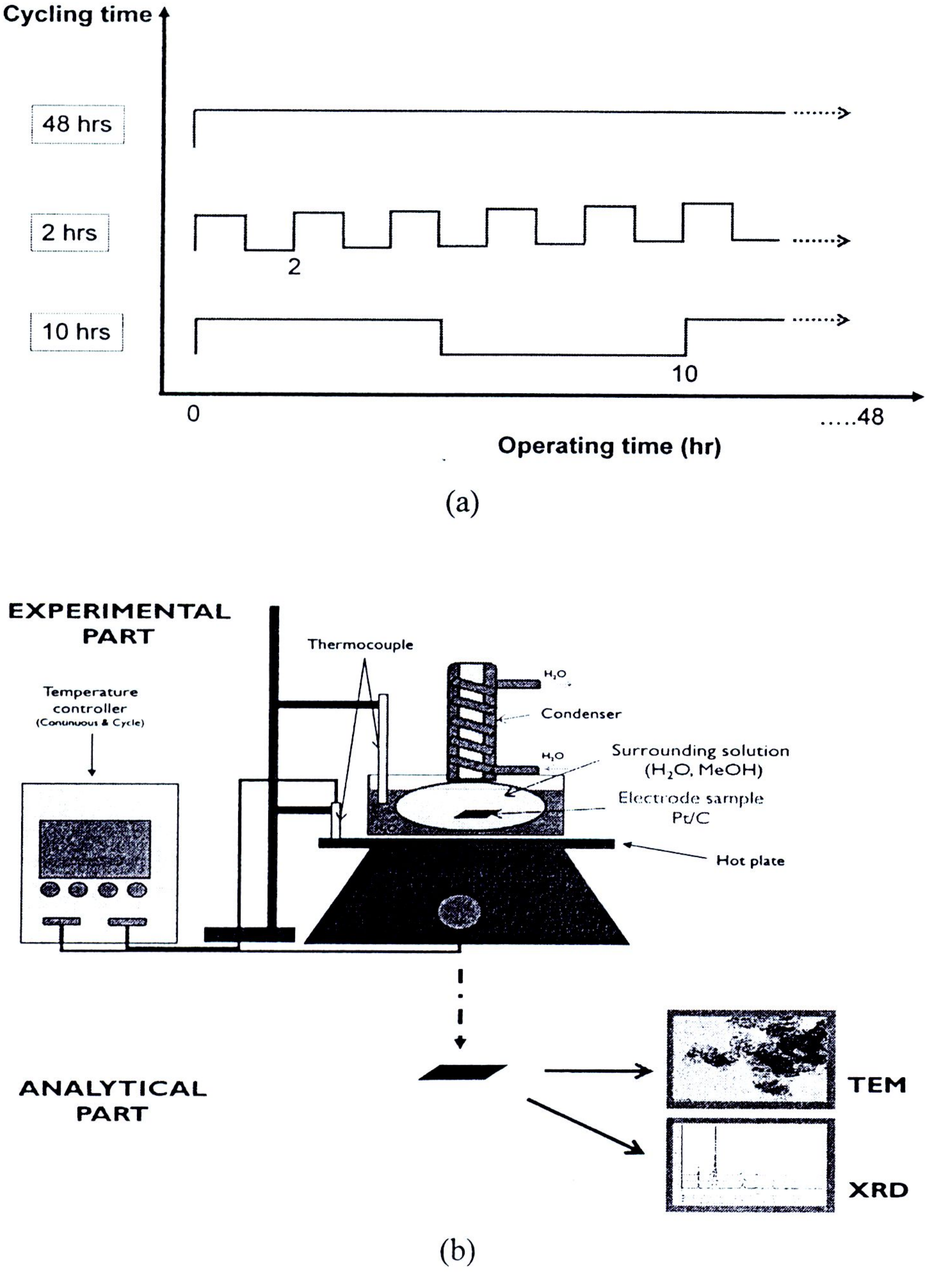


Figure 3.2 Schematic diagram of the experimental set up as methanol-oxygen operation.

For the second part, the proving of thermal cycling on agglomeration of Pt electrocatalyst was performed. A commercial gas diffusion electrode (GDE) containing with 20 wt% Pt/Vulcan XC-72 and loading 1 mg Pt cm^{-2} (Electrochem) with the size of 1 x 1 cm^2 was used in this experiment. The deionized (DI) water and methanol solution (1 M) were studied. The temperatures of 60 and ~100°C were selected for DI water while 60°C was chosen for methanol solution. In the cycle operation, the catalyst electrode was exposed to DI water or methanol solution 1 hr then exposed at room temperature for 1 hr, a temperature at this tested cycle was operated for 48 hr. In addition, with DI water surrounding, the both cycle period of cycle 2 and 10 hr was investigated. The cycle period of 2 hr or 10 hr meaning that the catalyst was immersed in DI water or methanol for 1 hr or 5 hr at applied temperature and then stop for 1 hr or 5 hr, respectively (figure3.3 (a)). The period of exposure was varied to explore the acceleration of catalyst particle agglomeration. Another environment of methanol solution was studied. The loss of specific surface area was also reported with the results from TEM and XRD as display in figure3.3 (b).



(a)

(b)

Figure 3.3 (a) Operating pattern of thermal cycling and (b) schematic diagram of an experimental part and an analytical part in the section of Pt electrode.

Moreover, the membrane electrode assembly (MEA) consisting of the commercial electrodes of Pt and a Nafion® 115 membrane were fabricated. Both anode and cathode electrodes were prepared by using the GDE (Electrochem) loading of 1 mg Pt cm^{-2} with the size of 5 cm^2. The MEA was hot-pressed at 150 °C and 300 psi for 90 sec. The MEA was activated under a hydrogen flow and an oxygen flow at anode and cathode for 24 hrs, respectively. After that, the MEA was fed with 2 ml min^{-1} of 1 M methanol solution and 100 ml min^{-1} O_2 at ambient pressure to the anode and the cathode, respectively. The cycle period of fuel/oxidant feeding and cell temperature was 3 hr start and 3 hr stop at the cell temperature at 60°C within 15 hr day^{-1} as shown in Figure 3.4. The polarization or V-I curve was measured during cycle operation for 4 days.

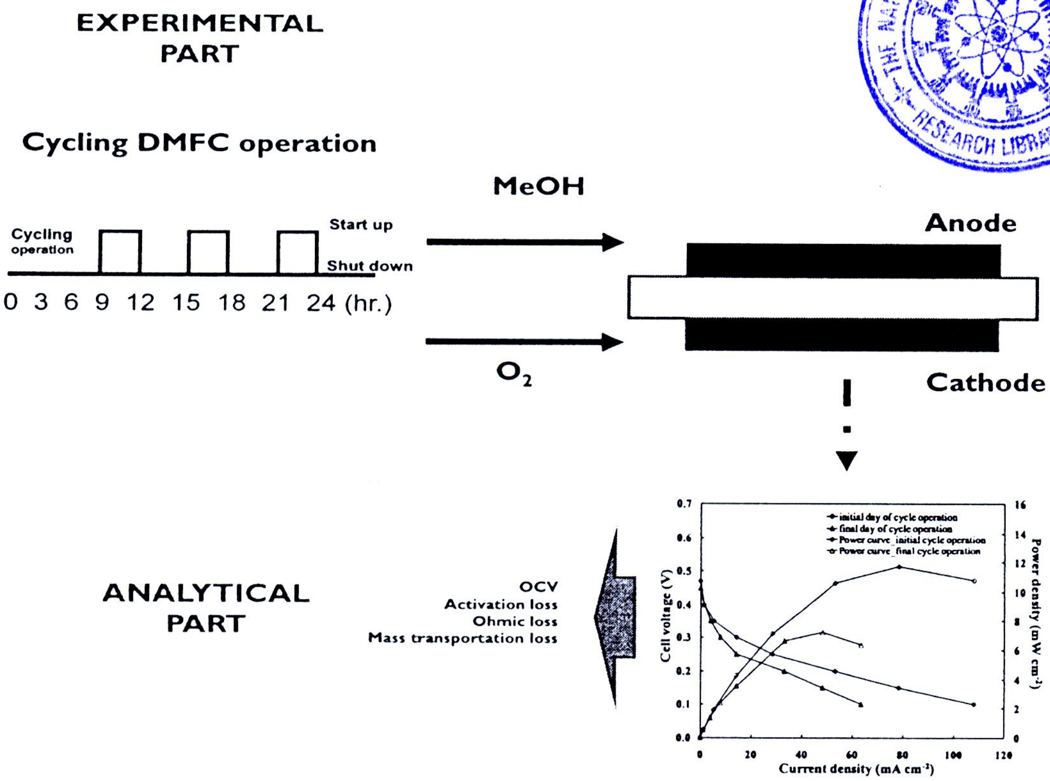


Figure 3.4 Schematic diagram of an experimental part and an analytical part in the section of MEA operated under cycling operation.

3.1.2 Methanol-Air system

For the second part, in the methanol-air system, the cell was operated under step-cycling operation mode and long-run mode for 100 hr, designated as SCO and LR-100, respectively. The SCO mode was determined with long-term operation for 100 h under the step drawing current condition of load profile as shown in Figure 3.5. This leveling load condition represents the change of load profile during operating time depending on the demand of users for real DMFC operation with methanol circulated and air fed. For this experiment, the load profile was set as the cycling step of drawing current from low to high and high to low of current density. Each step of the cycling operation after drawing current, the load profile was changed to open circuit voltage (OCV). For this experiment, the feeding of fuel and oxidant, and, heating of cell were constantly supplied while the load profile was varied from 300 mV down to 100 mV and again up to 300 mV within period of 10 h. The continuous drawing current at 300 mV during 100 h was set as the base case to compare the cell performance loss during testing period. Moreover, this operation was assumed as real, operating with air and circulation of methanol solution. Then, this experiment was cut of pre-heater and humidifier for fuel and oxidant as shown the test station diagram in Figure 3.6.

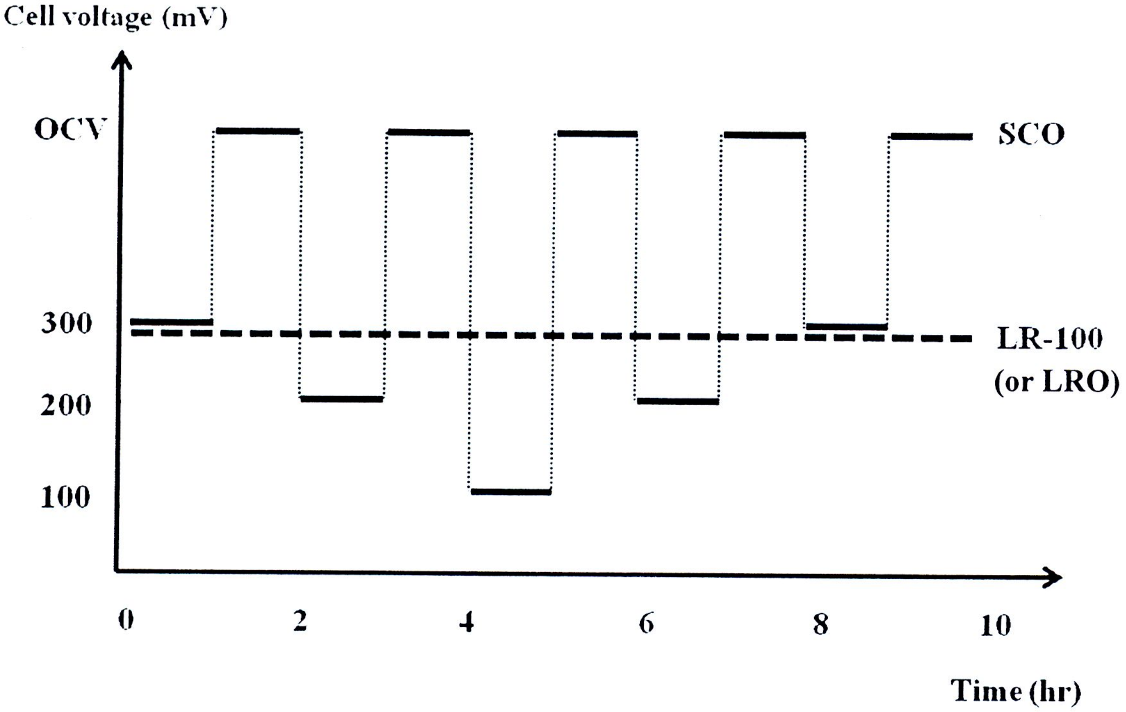


Figure 3.5 Diagram of operational mode of SCO and LR-100h.

For the preparation of MEA, catalyst inks were prepared in an ethanol solution and a 15 % Nafion® ionomer solution with 40 wt % Pt and 20 wt % Ru supported on carbon (Alfa Aesar) for the anode ink and with 60 wt % Pt/C (Alfa Aesar) for the cathode catalyst ink. The catalyst inks were sonicated for 20 mins and then sprayed on a 5 cm^2 gas diffusion layer (GDL: H2315IX53C173 (Vildona)) to obtain the loading of 1 mg cm^{-2} Pt catalyst.

Also, 0.5 mg/cm^2 of Nafion® solution was sprayed on both anode and cathode catalyst layers. Then, they were hot-pressed for 3 mins onto both sides of a Nafion® 117 membrane at 130 °C and 50 kg cm^{-2} in order to form a membrane electrode assembly (MEA). The MEA was tested with a 5 cm^2 active area cell. The cell was pre-conditioned with flowing the circulated deionized water (DI) water to both anode and cathode sides of the cell at 60 °C. At the 3rd day, methanol solution (1.0 mol m^{-3} (M)) and air were passed through the anode and cathode at 80°C, respectively, and current was drawn from the cell at cell voltage of 0.6 V for 15 seconds. Then a repeating of 16 cycles of cell conditioning at 0.15 V for 60 sec and 0.6 V for 15 sec was applied for cleaning surface of catalyst and pore of carbon as an activation process. After this step, the cell temperature was reduced to 70°C and the current was drawn from the cell starting at 0.3 V for 600 sec followed and then at 0.6 V for 300 sec and 0.3 V for 120 sec. After this the cell polarization behavior was measured with a single CV cycle from OCV to 100 mV. Furthermore, the cell was continuously drawn current with 20 cycles of 0.4 V for 10 min and 0.2 V for 10 min. Finally the cell was left overnight at 30 °C without any load applied. At the 4th day the DMFC was started to operate under the test cycling condition. During the life-test, the single cell was tested by feeding a methanol solution (1 mol L^{-1}) and oxygen into the anode and cathode at a flow rate of 2.8 mL min^{-1} and 150 mL min^{-1}, respectively. The current density decaying at constant voltage was collected and the degradation of cell performance curve was recorded during test time.

For both SRS mode and SCO modes, the cell performance degradation during test time by using potentiostat as an electronic load was measured. The cell polarization was recorded and the power density loss from the initial value of each mode was compared. Moreover, the effect of cycling operation was further explored on the fading behavior during long-term operation using in-situ and ex-situ techniques.

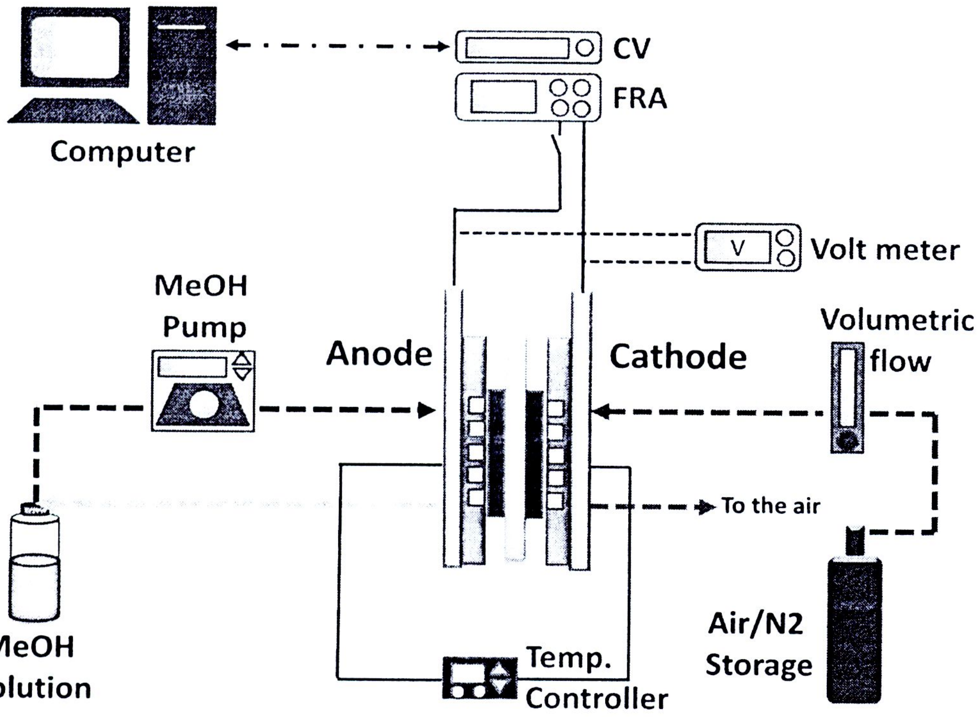


Figure 3.6 Schematic diagram of the life-test as methanol-air operation.

3.2 Characterization

This part was performed to investigate the cause of cell performance degradation which was affected by mode of cycling operation with in-situ and ex-situ techniques. These techniques of linear sweep and cyclic voltamogram, frequency response analysis, and electron spectroscopy as TEM, XRD, and EDX were employed to explore the fading behavior of the DMFC that experienced cycling operation. The MEA sample from each operating condition was characterized using different techniques mentioned above to obtain both the same and different information. Moreover, the complex cause of DMFC performance degradation was detected and interpreted.

3.2.1 In situ methods

The measure of polarization, linear sweep voltammogram, frequency response analysis, and cyclic voltammogram were applied as *in situ* methods on both cases of the

SRS mode and the SCO mode and also then compared with the LR mode for the cell degradation test. The details of these in situ methods were noticed below.

(1) Cell polarization

For the SRS mode, the single cell polarization was performed at 80 °C and also, the anode was fed with 1 mol L^{-1} methanol at a flow rate of 1 mL min^{-1} without backing pressure and the cathode was fed with humidified O_2 with a flow rate of 180 ml min^{-1} at 1 bar backpressure. For the SCO mode, the single cell performance curve was measured at 70 °C with the anode fed of 1 mol L^{-1} methanol at a flow rate of 2.8 mL min^{-1} without backing pressure and the cathode fed with non-humidified air with a flow rate of 150 sccm at no backpressure.

The curve of cell polarization was measured with the electronic load (Agilent N3301A-N3304A) and the potentiostat (ACM GillAC) for the mode of SRS and SCO, respectively. The cell current was drawn from OCV to 0.1 V with a step potential of 0.05 V per point for the electronic load and 20 mV s^{-1} for the potentiostat. And then the V-I curve was plotted. The decreasing value of OCV represents the methanol crossover. For the V-I curve, at the low current density, this shows the effect of an activation loss. Furthermore, an ohmic loss and a mass transport loss can observe at the region of medium and high drawing current density, respectively.

(2) Anode polarization

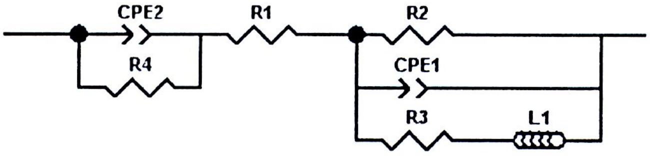
For the SCO mode, the linear sweep voltammogram was used to measure the anode polarization. The anode side which circulated feed with 1 mol L^{-1} methanol at 2.8 ml min^{-1} without back pressure was set as the working electrode and the cathode which fed with N_2 at 50 ml min^{-1} for 10 min before the test was performed to be the reference electrode as relative hydrogen electrode (RHE). After that the anode potential was investigated with scan rate at 5 mV s^{-1} starting at 0 V versus RHE and ending until current reached about 250 mA cm^{-2}. The increasing value of anode polarization replies to the surface electrode problem such as the activation loss from the catalyst agglomeration.

(3) Cell Impedance

During the life-test, for the SRS mode, a frequency response analysis (FRA) was used for evaluating cell impedances under the condition of DC potential 0.4 V and AC amplitude 10 mV with the record of 10 points per decade from 5 kHz to 0.05 Hz under a Solatron 1260 frequency response analyzer. Then the Nyquist plots obtained were analyzed with an equivalent circuit model as shown in Table 3.1.

However, for the SCO mode, a FRA was used for evaluating cell impedances under the condition of DC potential 0.4 V and AC amplitude 10 mV with the record of 10 points per decade from 5 kHz to 0.05 Hz under a ACM instrument model GillAC. Then the Nyquist plots obtained were analyzed with only the change value of Rs and Rct at high frequency and the distortion of Niquist curve at low frequency.

Table 3.1 The definition of equivalent circuit components.

Component	**Definition of equivalent circuit** 
R1	the internal resistance (membrane, electrode and interface resistance)
R2	the charge-transfer resistance at the interface of catalyst at anode or a methanol electro-oxidation reaction resistance
CPE1	a capacitive component including diffusion effect at anode (use in a model in place of a capacitor to compensate for nonhomogeneity in the system) - CPE-T: capacitance - CPE-P: nonhomogeneity constant
R3	an electro-oxidation reaction resistance of CO_{ads}
L	an inductive element which induces phase delay by slow reaction of CO_{ads}
CPE2	a capacitive component including diffusion effect at cathode
R4	the charge-transfer resistance at the interface of catalyst at cathode or a oxygen reduction reaction resistance

(4) Methanol striping

The methanol stripping method was performed in three steps of measurement as described below:

(1) A 1 mol L^{-1} methanol solution was fed to the anode side at a flow rate of 1 mL min^{-1} at 80 °C as the working electrode and, for the SRS mode, H_2 was applied at the cathode side to perform the dynamic hydrogen electrode (DHE) as the reference. The anode potential was operated under the voltage of 0.1 V versus DHE for 20 min. But, for the SCO mode, the reference was set as a relative hydrogen electrode (RHE) by feeding N_2 to cathode side before test.

(2) De-ionized water was fed to remove the unadsorbed methanol with a flow rate of 2 mL min^{-1} for 20 min to while the anode potential was held at 0.1 V versus DHE for 20 min at the same temperature of 80°C.

(3) The cyclic voltammogram was applied during the anode potential was cycled between 0.1 and 0.7 V versus DHE at 20 mV s^{-1} for five cycles, and the first and fifth cycles were recorded.

3.2.2 Ex-situ methods

The measure of X-ray diffraction, transmission electron microscopy, and energy dispersive X-ray spectroscopy were used as *ex situ* methods on the SRS mode for exploring the fading of electrode structure before and after test time. The details of these ex-situ methods were noticed below.

To get an electrode catalyst sample for measuring with three ex-situ methods, the membrane electrode assembly was soaked in methanol solution at high concentration. After that, both anode and cathode electrodes were peeled out from Nafion® membrane by themselves. The anode and cathode catalyst powder was detached from electrode backing by using the blade. Then, each electrode catalyst powder was dissolved in ethanol solution and sonicated for 15 min then sample slurry was dropped on a holey polyvinyl formal microgrid. The dried powder catalyst on the top of microgrid was a sample that ready to measure the chemical structure of the electrocatalyst.

(1) X-ray diffraction (XRD)

This analysis is carried out on a Bruker:Discover D8 System equipped with a Cu Kα radiation and a graphite filter. The monochromatic condition was set at tube voltage of 40 kV and tube current of 4 mA. The range of 2θ angular regions was set between 10° and 90°. Patterns are obtained at a scan rate of 5°/min with step of 0.02°. For the XRD patterns, the mean particle sizes was calculated according to Scherrer's formula $L = \frac{0.9\lambda_{K\alpha_1}}{\beta_{2\theta}\cos\theta_{max}}$ where $\lambda_{K\alpha_1}$is the wavelength of X-ray (1.5418 Å), θ_{max} the angle at the peak maximum, and $B_{2\theta}$ is the width (in rad) of the peak at half height.

(2) Transmission electron microscopy (TEM)

This analysis was carried out on a JEOL JEM-2 (010microscope). The tube system was operated at 80 - 200 keV. The images of catalyst particles on carbon were captured at the magnification of 50,000 and 150,000. For the TEM images, the size diameter and size distribution were measured and then shown as a histrogram for each sample. Moreover, the specific surface area (SSA) of the catalyst particles was calculated by equation of $s = \frac{6\times10^4}{\rho d}$ where ρ is the metal density (ρ_{Pt} = 21.45 g cm^{-3}) and d is the mean particle size in Å which assume that all of the metal particles are spherical in shape.

(3) Energy dispersive X-ray spectroscopy (EDX)

This analysis was carried out on a Phillips, Model XL-30 as a X-ray detector. The working system voltage was operated at 20 kV. The digital data of EDX were resulted as a percentage of atomic on material content in the catalyst sample. For the EDX data, the change of Pt:Ru atomic ratio was determined before and after test time.