CHAPTER 5 CONCLUSIONS AND RECOMENDATIONS

5.1 Conclusions:

The study of direct methanol fuel cell degradation during cycling operation was performed and compared to continuous operation. The aging determination of the effect on different operations was carried out in both Methanol-O_2 and Methanol-Air. Moreover, the case study for reduction of performance loss was done by using PtRu-PtSn/C catalyst and mixed methanol/ethanol.

Methanol-O_2 system

The investigation of fading behavior of DMFCs under a SRS operation was carried out by simulating a real application condition as power generating systems for portable electrical devices in order to identify the causes of DMFC degradation and its severity and to compare it with the system tested in a long-time operational mode. It was found that the SRS condition severely decayed the cell performance more than the LR operation performed for the same running period (45 h). The cell performance decay under the SRS mode was 12% more than that under the LR mode. Characterization of fuel cells and electrocatalysts indicated that the major reasons for degradation of DMFC under the SRS mode were ascribed to the sintering of metal particles and Ru-dissolution. Both TEM and XRD results demonstrated that the increase of average size of PtRu catalysts for the case of SRS operation was 16% and 18%, respectively, higher than the LR operation. Furthermore the EIS results showed that the ARR increased from the initial value of 0.26 Ω cm^2 to 0.30 Ω cm^2 after operating under the SRS mode for 5 days (45 h running time). Comparing to previous life-test data of non-stop operation, the increase rate of ARR in a SRS operation was faster, verifying the different degrees of severity of the operational modes on DMFC performance.

Moreover, in the cases of using the Pt electrode as anode, the cycle operation accelerated the growth of Pt catalyst particle size especially in methanol solution environment through the migration of the crystal under the different chemical stress with methanol oxidation during cycling operation. With liquid methanol fed on the Pt catalyst electrode at anode of the MEA, the cell performance degradation was caused by the loss of catalyst surface area due to particle agglomeration and the reduction of OCV due to fuel crossover.

Methanol-Air system

The investigation of cell performance behaviour under the step cycling operation mode (SCO) was carried out to simulate a practical application condition for portable devices. To identify the causes of DMFC degradation and to compare it with the cell tested under a long running operation (LRO) mode for 100h, the single cell was tested for its performance loss and characterized by using in-situ techniques. For 100 h of the degradation test, the SCO mode decayed the cell performance higher than the LRO mode although the current drawing time of the SCO mode was half of that of the LRO mode. The loss of power density was 73.9% and 58.8% for SCO and LRO modes, respectively. Characterization of DMFC anode and cathode indicated that the major causes of performance degradation under the SCO mode were ascribed to the Ru dissolution of the anode catalyst and the higher cathode polarization resulting from methanol crossover. Furthermore the FRA results revealed a distortion of Nyquist plot at low frequency end resulting from a loss of Ru and a reduction of internal resistance. The main cause of cell degradation was catalyst deterioration instead of ohmic resistance.

Reduction of the cell performance loss

The DAFC performance with various mixed methanol/ethanol fuels was investigated. Two types of membrane-electrode assemblies (MEAs) consisting of different anode catalysts, PtRu-PtSn/C and PtRu/C, were fabricated and studied. It was found that the cell performance decreased drastically even at low content of ethanol in the mixed fuels (up to 10% by volume of ethanol) and gradually reduced and approached that of the direct ethanol fuel cell (~15-20 mW/cm^2). Although the mixed alcohol could be oxidized at many different potential values, the current density produced from these reactions was decreased due to the slow electrooxidation of ethanol. By comparing the results of the mixed alcohol solution feed with those of methanol and ethanol solutions on three different electrodes, PtRu/C, PtSn/C and mixed PtRu-PtSn/C, it can be explained that the drop of cell performance in mixed fuel could be caused by the competitive adsorption of ethanol on PtRu/C due to the steric hindrance effect (ethanol is larger than methanol), and ethanol could compete with methanol for the adsorption on Pt active sites. From the performances of PtRu-PtSn/C and PtRu/C cells operated with mixed alcohol fuels, PtRu/C showed higher performance than PtRu-PtSn/C since the ohmic resistance of PtRu/C was less than PtRu-PtSn/C. Thereby, PtRu/C was the most suitable catalyst for mixed alcohol fuels.

5.2 Recommendations:

This research gives an understanding of fading behavior and cause of DMFC performance degradation under the cycling operation. In Methanol-O_2 and Methanol-Air systems, both cycling operations of SRS and SCO caused the methanol crossover, the catalyst agglomeration, the Ru dissolution and crossover, and the swelling of membrane. These causes of degradation should be further investigated with the method of AC voltammogram which integrated between the techniques of CV an FRA. The excellent report can be obtained and give a new way to interpret the loss of cell performance during test time without shutting down the system.

To prevent the degradation of MEA under cycling operation with methanol fuel, the activity of catalyst should be improved by preparing a new metal type of catalyst that can be formed as a good metal alloy or using a new catalyst support to reduce the leaching of unalloy Ru. To prevent the metal crossover, the Nafion® membrane should be replaced with a new type of membrane such as Polybenzimidazole (PBI) and then operate the cell under the system of alkaline. Since, PBI polymer exhibits excellent chemical and thermal stability and stability towards acids and bases, then it can be used for operating under the alkaline system that can serve the reduction of dissolution of Ru more than in an acid system, and can reduce the fuel crossover cause from PBI does not rely on water, then, the crossover of Ru will be reduced. To prevent the agglomeration of catalyst particles, a method to be carried out is do not operating the cell at high temperature and keeping operation at continuous mode under a suitable drawing current density condition.