

ห้องสมุดงานวิจัย สำนักงานคณะกรรมการการวิจัยแห่งชาติ



E42130

**AN INVESTIGATION OF DIRECT METHANOL FUEL CELL DEGRADATION
DURING CYCLING OPERATION**

MR. NUTTHAPON WONGYAO

ID: 48920004

**A THESIS SUBMITTED AS A PART OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
IN ENERGY TECHNOLOGY**

**THE JOINT GRADUATE SCHOOL OF ENERGY AND ENVIRONMENT
AT KING MONKUT'S UNIVERSITY OF TECHNOLOGY THONBURI**

2ND SEMESTER 2010

COPYRIGHT OF THE JOINT GRADUATE SCHOOL OF ENERGY AND ENVIRONMENT

600256255

ห้องสมุดงานวิจัย สำนักงานคณะกรรมการการวิจัยแห่งชาติ



**AN INVESTIGATION OF DIRECT METHANOL FUEL CELL DEGRADATION
DURING CYCLING OPERATION**

**MR. NUTTHAPON WONGYAO
ID: 48920004**



**A THESIS SUBMITTED AS A PART OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
IN ENERGY TECHNOLOGY**

**THE JOINT GRADUATE SCHOOL OF ENERGY AND ENVIRONMENT
AT KING MONGKUT'S UNIVERSITY OF TECHNOLOGY THONBURI**

2ND SEMESTER 2010

COPYRIGHT OF THE JOINT GRADUATE SCHOOL OF ENERGY AND ENVIRONMENT

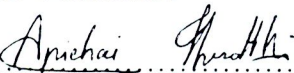
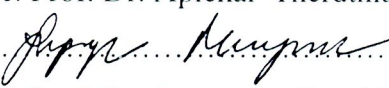
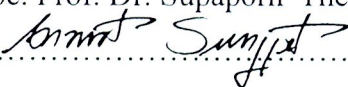
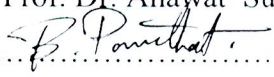
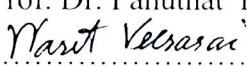
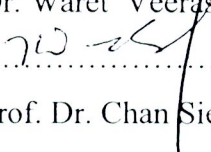
An Investigation of Direct Methanol Fuel Cell Degradation During Cycling Operation

Mr. Nutthapon Wongyao
ID: 48920004

A Thesis Submitted as a Part of the Requirements
for the Degree of Doctor of Philosophy
in Energy Technology

The Joint Graduate School of Energy and Environment
at King Mongkut's University of Technology Thonburi
2nd Semester 2010

Thesis Committee

 (Assoc. Prof. Dr. Apichai Therdthianwong)	Chairman
 (Assoc. Prof. Dr. Supaporn Therdthianwong)	Co-Chairman
 (Assoc. Prof. Dr. Anawat Sungpet)	Member
 (Assist. Prof. Dr. Panuthat Boonpramuk)	Member
 (Dr. Waret Veerasai)	Member
 (Prof. Dr. Chan Siew Hwa)	External Examiner

Thesis Title: An Investigation of Direct Methanol Fuel Cell Degradation During Cycling Operation.

Student's name: Mr. Nutthapon Wongyao
Organization: The Joint Graduate School of Energy and Environment (JGSEE)
Telephone: 02-4708000 ext 500
Fax Number: 02-4709325
E-mail: w_nutthapon@hotmail.com

Supervisor's name: Assoc. Prof. Dr. Apichai Therdthianwong
Organization: Fuel Cells and Hydrogen Research and Engineering Center
King Mongkut's University of Technology Thonburi (KMUTT)
Telephone: 02-4708000 ext 404
Fax Number: 02-8729118
E-mail: apichai.the@kmutt.ac.th

Overseas Collaborator's name: Prof. Keith Scott
Organization: School of Chemical Engineering and Advanced Materials
Newcastle University (UK)
Telephone: +44 222 8771
E-mail: k.scott@ncl.ac.uk

Topic: An Investigation of Direct Methanol Fuel Cell Degradation During Cycling Operation

Name of student: Mr. Nutthapon Wongyao

Student ID: 48920004

Name of Supervisor: Assoc. Prof. Dr. Apichai Therdthianwong

Abstract

E 42130

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). Ex-situ methods of X-ray diffraction (XRD), transmission electron microscopy (TEM), and energy dispersive X-ray spectroscopy (EDX) were used to determine the catalyst's particle sizes and compositional change. Also, in-situ methods of frequency response analysis (FRA), and cyclic voltammetry (CV) were used to identify the loss of cell performance during test-time. The MEA performance loss with methanol-oxygen system was investigated and compared between the long-running (LR) and the start-run-stop (SRS) as a cycling operation for 45 h. The maximum cell power density was reduced approximately by 20% and 32% of the initial value after operating under the LR and the SRS modes, respectively. This result corresponded to the anode catalyst agglomeration data obtained from both XRD and TEM analyses with higher increases of PtRu particle sizes under the SRS operation. In addition, the FRA spectra revealed that the anode reaction resistance increased from the initial value of $0.26 \Omega/\text{cm}^2$ to $0.30 \Omega/\text{cm}^2$ after life-testing under the SRS mode for 45 hr. A right-shift of the methanol oxidation peak and a 5.0% reduction of electrocatalyst surface area observed from the cyclic voltammograms also supported this finding. Finally, the decay of cell performance was due to the Ru crossover, as verified by EDX results. Moreover, a 100 h non-stop methanol-air feed system was carried out and the anode dissolution indicated a decrease in the active catalyst area having been caused by Ru dissolution. Cathode performance loss and Nafion[®] membrane swelling were caused by severe methanol crossover.

Keywords: Direct methanol fuel cell, Cycle operation, Performance degradation, Methanol crossover, Anode dissolution.

ACKNOWLEDGMENTS

First, the author would like to express thanks to his advisor, Assoc. Prof. Dr. Apichai Therdthianwong, and co-advisor, Assoc. Prof. Dr. Supaporn Therdthianwong, who gave me a chance to study in the Ph.D. program, a deep knowledge on fuel cell fundamentals and more techniques to prepare and operate fuel cells as well as guiding me on this study. Moreover, thanks to their kindness in providing me all financial and equipment support, and also, their ideas, suggestions, recommendations and time. Second, the author would like to thank the Joint Graduate School of Energy and Environment (JGSEE), the Fuel Cells and Hydrogen Research and Engineering Center of King Mungkut's University of Technology Thonburi (KMUTT), the Royal Golden Jubilee (RGJ) program of the Thailand Research Fund (TRF) for an academic scholarship and instrument support.

Furthermore, for the overseas extended research, this work was supported by the Fuel Cell Research group, School of Chemical Engineering and Advanced Materials, Newcastle University and the Royal Golden Jubilee (RGJ) program of the Thailand Research Fund for an academic scholarship. Also, the author would like to thank Prof. Keith Scott, Dr. S. M. Senthil Kumar, Dr. Mohamed Mamlouk and Mr. Georgios Vlachogiannopoulos for their concept idea of research and technical support. In addition, special thanks to Miss Krongthong Kamonsuangkasem for her service support and contact.

Moreover, this work would not have completed without the support of my family and over people around me who have been waiting for my success.

CONTENTS

CHAPTER	TITLE	PAGE
	ABSTRACT	i
	ACKNOWLEDGEMENT	ii
	CONTENTS	iii
	LIST OF TABLES	v
	LIST OF FIGURES	vii
1	INTRODUCTION	1
	1.1. Rational/Problem Statement	1
	1.2. Literature Review	3
	1.3. Research Objectives	7
2	THEORIES	10
	2.1 Fuel cell	8
	2.2 Direct methanol fuel cell (DMFC)	19
	2.3 Characterization techniques of electrode and MEA performance	22
3	METHODOLOGY	36
	3.1 System operation	36
	- <i>Methanol-O₂ system</i>	36
	- <i>Methanol-air system</i>	40
	3.2 Characterization	43
	- <i>In-situ methods</i>	43
	- <i>Ex-situ methods</i>	46
4	RESULTS AND DISCUSSION	48
	4.1 Methanol-O ₂ system	48
	- <i>DMFC performance test under different operating mode of SRS and LR</i>	48
	- <i>The causes of DMFC degradation on methanol-O₂ system</i>	50
	- <i>Effect of thermal cycling operation on agglomeration of Pt electrode</i>	61

	4.2 Methanol-air system	70
	- <i>The degradation of DMFC performance operation with SCO</i>	70
	- <i>Comparison of DMFC performance operated under different modes</i>	79
	4.3 Reduction of the cell performance loss	94
	- <i>PtRu-PtSn/C cell performance with mixed alcohol fuels</i>	94
	- <i>Performance of direct alcohol fuel cells using PtRu-PtSn/C, PtRu/C and PtSn/C catalysts fed with pure alcohol solutions</i>	100
	- <i>Performance of the PtRu/C cell fed with mixed alcohol solutions</i>	104
5	CONCLUSION AND RECOMMENDATION	107
	5.1 Conclusions	107
	5.2 Recommendation	109
	LIST OF REFERENCES	110
	APPENDIX	122

LIST OF TABLES

TABLES	TITLE	PAGE
2.1	The component and function of membrane electrode assembly	13
2.2	The category of fuel cell by operating property	17
2.3	The category of fuel cell by chemical reaction	18
2.4	The categories of fuel cell by typical application	18
2.5	The comparison of electrochemical reaction between PEMFC and DEMFC	20
2.6	The definition of impedance analysis element for DMFC	27
3.1	The definition of equivalent circuit components	45
4.1	The equivalent circuit component values during start-run-stop operation	52
4.2	Particle size and specific surface area loss of the Pt/C catalysts surrounded with DI water	63
4.3	The value of anode onset potential, Tafel slope and exchange current density for SCO mode	74
4.4	Anode peak currents and position of methanol oxidation at different test times of the SCO mode	76
4.5	Cell impedance at different test times of the SCO mode	78
4.6	Comparison of cell performance degradation rate between SCO and LR-100 modes	81
4.7	The cell parameter value of open circuit voltage, exchange current density, area specific resistance, and maximum power density during test time	83
4.8	The value of anode onset potential at mode of SCO and LR-100	88
4.9	The value of anode Tafel slope and exchange current density (i_0)	90
4.10	The value of anode internal resistance (R_s) and charge transfer resistance (R_{ct})	93
4.11	Anode reaction resistance, charge transfer resistance and internal resistance of PtRu-PtSn/C anode operated with various mixed fuel ratios	99

LIST OF TABLES (Cont')

TABLES	TITLE	PAGE
4.12	Anode reaction resistance, charge transfer resistance and internal resistance of PtRu/C anode with various mixed fuel ratios	105

LIST OF FIGURES

FIGURE	TITLE	PAGE
1.1	The complex causes of DMFC degradation diagram	5
2.1	The fuel cell reaction at a) anode, b) cathode, and c) the overall reaction	13
2.2	The pathway of methanol oxidation	21
2.3	Sinusoidal Current Response in a Linear System	23
2.4	Origin of Lissajous Figure	24
2.5	Nyquist Plot with Impedance Vector	25
2.6	Simple Equivalent Circuit with One Time Constant	25
2.7	Linear potential sweep of cyclic voltammetry	28
2.8	Oxidation current with forward and backward sweep	28
2.9	The response curve of CV by electrochemical reaction step which depend on potential scan	31
3.1	Diagram of operational mode per day of SRS and LR	37
3.2	Schematic diagram of the experimental set up as methanol-oxygen operation	38
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	39
3.4	Schematic diagram of an experimental part and an analytical part in the section of MEA operated under cycling operation	40
3.5	Diagram of operational mode of SCO and LR-100h	41
3.6	Schematic diagram of the life-test as methanol-air operation	42
4.1	Comparison of performance of the 5 cm ² cell active area for 5 days operation between the SRS and LR mode conditions.	49
4.2	Frequency response analysis for the DMFC under SRS operation on different life-test days: (a) impedance curves, (b) impedance value at high frequency and (c) equivalent circuit model.	51

LIST OF FIGURES (Cont')

FIGURE	TITLE	PAGE
4.3	Polarization curves of the DMFC operated in SRS mode for six days	54
4.4	Cyclic voltammogram scan curves before and after life-testing in SRS operational mode	55
4.5	XRD patterns of the PtRu/C anode catalysts and the Pt/C cathode catalysts: (a) before testing, (b) after life-test in LR operational mode, and (c) after life-test in SRS operational mode	57
4.6	TEM images and histograms of size distributions of the anode PtRu/C catalysts fed with methanol and cathode Pt/C catalysts fed with O ₂ at 80 °C: (a) before testing, (b) after life-test in LR mode, and (c) after life-test in SRS mode.	60
4.7	XRD patterns of Pt/C surrounded with DI water at different temperatures and cycle periods under cycle operation	62
4.8	TEM images and size distributions of the Pt surrounded by DI water under cycle operation (a) fresh Pt/C, (b) f = 2 h, 60°C, (c) f = 2 h, ~100°C and (d) f = 10 h, ~100°C	64
4.9	XRD patterns of Pt on C after exposure to methanol solution under cycle operation at different cycle parameters	65
4.10	TEM images of Pt on C after exposure to methanol solution under cycle operation at different cycle parameters	66

LIST OF FIGURES (Cont')

FIGURE	TITLE	PAGE
4.11	Cell performance curve at 1 st (initial) day and 4 th (final) day with liquid methanol and O ₂ feed on Pt electrode under cycle operation at anode and cathode, respectively	68
4.12	Cell performance curve at 1 st (initial) day and 4 th (final) day with H ₂ /O ₂ feed on Pt electrode after cycle feed with methanol	69
4.13	Performance curve interpretation with program STATISTICA version 6.0 to determine the activation loss (A) and the ohmic loss (r) value	69
4.14	Performances of DMFC single cell during 100 h test time with SCO mode	71
4.15	Polarization of cell operated with SCO mode, anode and cathode at 0 and 100 hr	72
4.16	Linear sweep potential of anode Pt-Ru/C catalyst at different test times during the SCO mode: (a) onset potential and (b) Tafel plot	74
4.17	Methanol-stripping test of anode Pt-Ru/C catalyst at different test times during the SCO mode	76
4.18	Cell performance comparison with different mode operation between LR-100 and SCO for a DMFC with 5 cm ² active area at the initial(0 h) and the final(100 h) test time: (a) V-I curve and (b) power density curve	80
4.19	The comparison of the variation in current density with time for a DMFC with 5 cm ² active area between operating mode of LR-100 at cell potential 300 mV and SCO at cell potential along load profile of 100, 200, and 300 mV	82
4.20	The comparison value trend of cell parameters during test time between LR-100 mode and SCO mode: (a) maximum power density and area specific resistance and (b) open circuit voltage and exchange current density	84

LIST OF FIGURES (Cont')

FIGURE	TITLE	PAGE
4.21	(a) Anode performance and (b) Cathode performance comparison with different test mode on LR-100 and SCO for 100 h	86
4.22	Comparison of linear sweep voltammogram of operation mode of SCO and LR-100 with temperature of 70° C (a) test time of 0 and 100 h, and also, the onset potential at different test times during test time of 100 h (b) SCO mode and (c) LR-100	88
4.23	Tafel plot during test time of 100 h (a) SCO mode and (b) LR-100	90
4.24	Complex plane plots of the anode impedance of PtRu/C electrode with AC amplitude 20 mV at operating DC 300 mV vs RHE under feed of 1 M CH ₃ OH during operating mode of (a) SCO and (b) LR-100.	93
4.25	Effect of the mixed fuel ratio on PtRu/C-PtSn/C electrode performance for DAFC operation: (a) polarization curve and (b) power curve.	95
4.26	(a) Linear sweep voltammogram of the fuel oxidation onset potential and (b) Cyclic voltammogram of mixed fuel stripping on PtRuSn/C electrode.	97
4.27	Impedance curves of the promoted Pt electrode-PtRuSn- at anode fed with various mixed fuels.	98
4.28	The equivalent circuit model for interpreting an impedance curve.	99
4.29	Maximum power density ratio and charge transfer resistance of PtRu-PSn/C catalyst for the anode on the DAFC performance	100
4.30	Effect of anode catalyst PtRu, PtSn, and PtRu-PSn on DAFC performance fed with: a) 1M methanol and b) 1M ethanol	102

LIST OF FIGURES (Cont')

FIGURE	TITLE	PAGE
4.31	Effect of mixed alcohol ratio on PtRu/C electrode performance: (a) polarization curve and (b) power curve	103
4.32	Comparison of maximum power density between PtRu-PtSn/C cell and PtRu/C cell operated with mixed alcohol solutions containing different ratios of 1M methanol/1M ethanol	105