

Copyright © Indian Institute of Technology

(Banaras Hindu University),

Varanasi - 221005, India.

All rights reserved

2021

CERTIFICATE

It is certified that the work contained in the thesis titled “**Development of Glycerol Based Microfluidic Fuel Cell**” by “**Deoashish Panjiara**” has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

It is further certified that the student has fulfilled all the requirements of Comprehensive Examination, Candidacy and SOTA for the award of Ph.D. Degree.

(Prof. Hiralal Pramanik)

Supervisor

Department of Chemical Engineering & Technology

Indian Institute of Technology

(Banaras Hindu University)

Varanasi – 221005, India

DECLARATION BY THE CANDIDATE

I, "**Deoashish Panjiara**", certify that the work embodied in this thesis is my own bona fide work and carried out by me under the supervision of "**Prof. Hiralal Pramanik**" from "July 2015 to March 2021" at the "Department of Chemical Engineering & Technology", Indian Institute of Technology (BHU), Varanasi. The matter embodied in this thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged and given credits to the research workers wherever their works have been cited in my work in this thesis. I further declare that I have not willfully copied any other's work, paragraphs, text, data, results, etc., reported in journals, books, magazines, reports dissertations, theses, etc., or available at websites and have not included them in this thesis and have not cited as my own work.

Date:

Place:

(DEOASHISH PANJIARA)

CERTIFICATE BY THE SUPERVISOR

It is certified that the above statement made by the student is correct to the best of my knowledge.

(Prof. Hiralal Pramanik)

Supervisor

Department of Chemical Engineering & Technology

Indian Institute of Technology

(Banaras Hindu University)

Varanasi -221005

Signature of Head of Department

(Prof. V. L. Yadav)

COPYRIGHT TRANSFER CERTIFICATE

Title of the Thesis: “Development of Glycerol Based Microfluidic Fuel Cell”

Name of the student: Mr. DEOASHISH PANJIARA

Copyright Transfer

The undersigned hereby assigns to the Indian Institute of Technology (Banaras Hindu University) Varanasi all rights under copyright that may exist in and for the above thesis submitted for the award of the “**Ph.D. Degree**”.

Date:

Place:

(Deoashish Panjiara)

Note: However, the author may reproduce or authorize others to reproduce material extracted verbatim from the thesis or derivative of the thesis for author's personal use provided that the source and the Institute's copyright notice are indicated.

Dedicated to My Beloved

Parents &

Family Members

ACKNOWLEDGEMENT

I take this opportunity to express my deep sense of gratitude through my heart to my esteemed supervisor **Prof. Hiralal Pramanik** who has helped enormously and always inspired me by his indispensable guidance and encouragement during the whole long research work. He has always supported and strengthened me in many direct and indirect ways. His thoughtful and valuable reviews, constructive criticism, and tireless review of the manuscript has immensely helped me to improve the work. I gratify him a lot of gratitude for showing confidence in my work and he gave me the freedom.

I also express my heartiest thanks to **Prof. V. L. Yadav**, Head of the Department, Department of Chemical Engineering & Technology, Indian Institute of Technology (BHU) for providing essential research facilities and encouragement during the research work.

I would especially thank Prof. P. Maiti and Prof. M.K. Mondal, Indian Institute of Technology, Banaras Hindu University. Without the help of them, my project may not be completed. I am very thankful for their valuable advice & guidance, **RPEC, DPGC members** of the Chemical Engineering & Technology Department for their useful suggestions during my research work at the institute. The instrumental facilities from CIFIC (IIT-BHU) Varanasi are gratefully acknowledged.

Also, I express my sincere thanks to all faculty members of the Department of Chemical Engineering and Technology, Indian Institute of Technology (Banaras Hindu University) for their continued help and co-operation in the completion of this research work.

I am very thankful to all technical and non-technical staff of the Department of Chemical Engineering & Technology, Institute of Technology, and Banaras Hindu University.

I also owe my sincerest thanks to my seniors and friends; Mr. Amit Kumar Rathoure, Mr. Pramendra Gaurh, Mr. Uday Guta, Mr. Satyansh Singh, Mr. Alok Singh Verma, Mr. Goutam Kishore Gupta, Mr. Abhay Kumar choudhary, Mr. Abhay Pratap Singh, Ms. Anjali Verma, Mr. Neeraj Yadav, and Ms. Saraswati Sonkar for their valuable help and support in the experiment, data analysis and presentation in the thesis as well as papers over the years.

The whole credit of my achievements goes to my father Late Chandra Shekhar Panjiara, mother Smt. Gita Devi, sisters Smt. Archana Bharti and Smt. Sindhu Snehi Bharti and brother Ashish Panjiara who were always there for me in my difficulties. It was their unshakable faith in me that has always helped me to proceed further.

Finally, I wish to extend warm thanks to all those who could not find a separate name but have helped directly or indirectly.

Above all, I am especially thankful to the Almighty God from whom I gathered the strength and perseverance during my research work.

Date:

Place: Varanasi

(Deoashish Panjiara)

TABLE OF CONTENTS

List of Figures

List of Tables

Nomenclature

Preface

CHAPTER 1	INTRODUCTION	1-11
CHAPTER 2	LITERATURE REVIEW AND OBJECTIVES	12-45
2.1	Literature review	12
2.1.1	Fundamentals of microfluidic fuel cell	12
2.1.2	Types of microfluidic fuel cell	16
2.1.3	Microfluidic fuel cell fabrication techniques	18
2.1.4	Components of microfluidic fuel cell	20
2.1.4.1	Electrode materials	21
2.1.4.1.1	Anode electrocatalyst for glycerol electrooxidation	21
2.1.4.1.2	Cathode electrocatalyst	23
2.1.4.1.3	Anode electrocatalyst preparation techniques	24
2.1.4.1.4	Electrochemical characterization	27
2.1.4.1.4.1	Electrochemical characterization of anode electrocatalysts	27
2.1.4.1.4.2	Electrochemical characterization of cathode	35
2.1.4.1.5	Physical characterization of anode electrocatalysts	37
2.1.4.1.5.1	X- ray diffraction	37
2.1.4.1.5.2	Scanning electron microscopy	38
2.1.4.1.5.3	Energy dispersive X- ray	38

2.1.4.1.5.4	Transmission electron microscopy	38
2.1.4.2	Cathode oxidant	39
2.1.4.3	Electrolytes	40
2.1.5	Cell performance	40
2.2	Objectives	45
CHAPTER 3	EXPERIMENTAL	46-61
3.1	Materials	46
3.2	Method	49
3.2.1	Bimetallic Pd-Pt/C electrocatalyst synthesis	49
3.2.2	Bimetallic Pd-Ni/C electrocatalyst synthesis	49
3.2.3	Physical characterization of electrocatalyst	50
3.2.3.1	X- ray Diffraction (XRD)	50
3.2.3.2	Scanning electron microscopy (SEM)/ Energy-dispersive X-ray spectroscopy (EDX)	50
3.2.3.3	Transmission electron microscopy (TEM)	51
3.2.4	Electrochemical characterization of electrocatalyst	51
3.2.4.1	Cyclic voltammetry (CV) analysis	51
3.2.4.2	Electrochemical impedance spectroscopy (EIS) study	52
3.2.5	Electrode preparation	53
3.2.6	Experimental Setup	54
3.2.6.1	Y-shaped air breathing microfluidic fuel cell	54
3.2.6.2	T-shaped air breathing microfluidic fuel cell	57
3.3	Evaluation of dimensionless numbers in MFC	60
3.4	Stability test of air breathing MFC	61

CHAPTER 4 OPTIMIZATION OF PROCESS PARAMETERS BY RSM	62-68
4.1 Introduction	62
4.2 Experimental procedures	65
4.3 Statistical analysis	65
CHAPTER 5 RESULTS AND DISCUSSION	69-181
5.1 Performance evaluation of Pd-Ni/C anode electrocatalyst: Part-I	70
5.1.1 Physical characterization	70
5.1.1.1 XRD analysis	70
5.1.1.2 SEM-EDX analysis	72
5.1.1.3 TEM analysis	74
5.1.2 Electrochemical study of anode	76
5.1.2.1 Cyclic voltammetry analysis	76
5.1.2.2 EIS analysis	78
5.1.3 Electrochemical study of cathode	81
5.1.3.1 Oxygen as oxidant	81
5.1.3.2 Mixed Oxidant	82
5.1.4 Performance evaluation of Pd-Ni/C anode electrocatalyst in MFC	84
5.1.4.1 Y-shaped air breathing MFC	84
5.1.4.1.1 Effect of flow rate at anode and cathode	84
5.1.4.1.2 Effect of anode electrocatalyst type	86
5.1.4.1.3 Effect of anode electrocatalyst loading	88
5.1.4.1.4 Effect of cathode electrocatalyst loading	89
5.1.4.1.5 Effect of anode KOH electrolyte concentration	91

5.1.4.1.6	Effect of cathode KOH electrolyte concentration	92
5.1.4.1.7	Effect of glycerol concentration	94
5.1.4.1.8	Effect of cell temperature	95
5.1.4.2	T-shaped air breathing MFC	97
5.1.4.2.1	Effect of flow rate at anode and cathode	97
5.1.4.2.2	Effect of anode electrocatalyst type	100
5.1.4.2.3	Effect of anode electrocatalyst loading	101
5.1.4.2.4	Effect of cathode electrocatalyst loading	103
5.1.4.2.5	Effect of glycerol concentration	104
5.1.4.2.6	Effect of anode KOH concentration	106
5.1.4.2.7	Effect of cathode KOH concentration	107
5.1.4.2.8	Effect of cell temperature	109
5.1.4.2.9	Bleaching and air as mixed oxidant for air breathing MFC	111
5.1.4.2.10	Different types of oxidants at cathode	113
5.2	Performance evaluation of Pd-Pt/C anode electrocatalyst:	115
	Part II	
5.2.1	Physical characterization	115
5.2.1.1	XRD analysis	115
5.2.1.2	SEM-EDX analysis	118
5.2.1.3	TEM analysis	120
5.2.2	Electrochemical characterization of electrocatalyst	123
5.2.2.1	Cyclic voltammetry of anode electrocatalysts	123
5.2.2.2	EIS study of synthesized anode electrocatalyst	125
5.2.3	Performance of Pd-Pt/C anode electrocatalyst in MFC	128
5.2.3.1	Y-shaped air breathing MFC	128

5.2.3.1.1	Effect anode electrocatalyst type	128
5.2.3.1.2	Effect of anode electrocatalyst loading	129
5.2.3.1.3	Effect of cathode electrocatalyst loading	131
5.2.3.1.4	Effect of anode KOH electrolyte concentration	132
5.2.3.1.5	Effect of cathode KOH electrolyte concentration	134
5.2.3.1.6	Effect of glycerol concentration	135
5.2.3.1.7	Effect of cell temperature	137
5.2.3.2	T-shaped air breathing MFC	138
5.2.3.2.1	Effect of anode electrocatalyst type	138
5.2.3.2.2	Effect of anode electrocatalyst loading	140
5.2.3.2.3	Effect of cathode electrocatalyst loading	141
5.2.3.2.4	Effect of glycerol concentration	143
5.2.3.2.5	Effect of anode KOH concentration	144
5.2.3.2.6	Effect of cathode KOH concentration	146
5.2.3.2.7	Effect of cell temperature	147
5.2.3.2.8	Bleaching and air as mixed oxidant for shaped air breathing MFC	148
5.2.4	Comparison of performance of synthesized electrocatalysts in Y-shaped and T-shaped MFC	151
5.2.5	Process Parameter Optimization Using RSM	155
5.2.5.1	ANOVA analysis and model development	155
5.2.5.2	Polarization and power density curves	160
5.2.5.3	Process parameter optimization and its effect on response	164
5.3	Evaluation of dimensionless numbers	171
5.3.1	Y-shaped air breathing MFC device	171
5.3.2	T-shaped air breathing MFC device	173

5.4	Comparison of present study with published work	175
5.5	Efficiency of the air breathing microfluidic fuel cell	179
5.6	Stability test of Y-shaped and T-shaped air breathing MFC	180
CHAPTER 6	CONCLUSIONS	182-188
6.1	Anode electrocatalyst characterization	183
6.1.1	Physicochemical characterization	183
6.1.2	Electrochemical characterization	184
6.2	Single cell performance	184
6.2.1	Y-shaped air breathing MFC	184
6.2.2	T-shaped air breathing MFC	185
6.2.3	Optimization of cell parameters using RSM	187
6.3	Future scope	188
	References	189
	Appendix A	203
	Appendix B	205
	Appendix C	207
	Appendix D	209
	Appendix E	211

LIST OF FIGURES

Figure 1.1	Schematic of a hydrogen/oxygen fuel cell and its reactions based on the proton exchange membrane fuel cell.	3
Figure 1.2	Schematic of microfluidic fuel cell.	5
Figure 2.1	An F-shaped air breathing microfluidic fuel cell captures oxygen from the surrounding air via gas diffusion through the ‘dry’ side of the porous cathode structure.	18
Figure 2.2	Glycerol electrooxidation mechanisms on Au and Pt electrodes in alkaline media.	28
Figure 2.3	CV curves in oxygen-saturated 2 M NaOH and KOH solutions at 298 K, respectively. Scan rate: 100 mV/s.	36
Figure 3.1	Schematic of three electrode cell assembly for performing CV and EIS studies with the help of potentiostat galvanostat (PGSTAT).	52
Figure 3.2	Glycerol transport pathway from bulk phase to the anode electrocatalyst layer and oxygen transport pathway from ambient to the cathode electrocatalyst layer.	54
Figure 3.3a	Schematic of Y-shape air breathing microfluidic fuel cell setup.	56
Figure 3.3b	Enlarge and detailed internal view of Y-shaped air breathing microfluidic fuel cell main unit.	56
Figure 3.4a	Schematic of T-shaped air breathing microfluidic fuel cell experimental setup.	59
Figure 3.5b	Enlarge and detailed internal view of T-shaped air breathing microfluidic fuel cell main unit.	59
Figure 3.5	Schematic of electrical circuit connections for measuring voltage current (V-I) data.	61
Figure 5.1	X-ray diffraction pattern of Pd-Ni/C with different weight ratios of metal.	70
Figure 5.2a	SEM-EDX images of synthesized Pd-Ni (16:4)/C electrocatalyst.	73
Figure 5.2b	SEM-EDX images of synthesized Pd-Ni (10:10)/C electrocatalyst.	73
Figure 5.2c	SEM-EDX images of synthesized Pd-Ni (4:16)/C electrocatalyst.	74
Figure 5.3a	TEM images and particle size distribution histogram of synthesized Pd-Ni (16:4)/C electrocatalyst.	75
Figure 5.3b	TEM images and particle size distribution histogram of synthesized Pd-Ni (10:10)/C electrocatalyst.	75

Figure 5.3c	TEM images and particle size distribution histogram of synthesized Pd-Ni (4:16)/C electrocatalyst.	76
Figure 5.4	Cyclic voltammetry for different ratios of Pd-Ni/C anode electrocatalyst in 1 M glycerol mixed with 1 M KOH at scan rate of 50 mV/sec; Temperature: 25 °C.	77
Figure 5.5a	Nyquist plots of synthesized electrocatalysts recorded at - 0.2 V in 1M glycerol mixed with 1M KOH solution; Temperature: 25 °C	79
Figure 5.5b	Equivalent circuit diagram corresponds to Nyquist plot.	80
Figure 5.6a	Cyclic voltammetry for 1 mg/cm ² Pt/C _{HSA} cathode in 1 M KOH in nitrogen purged solution at 50 mV/s scan rate; Temperature: 25 °C.	81
Figure 5.6b	Cyclic voltammetry for 1 mg/cm ² Pt/C _{HSA} cathode in 1 M KOH in an oxygen saturated solution at 50 mV/s scan rate; Temperature: 25 °C.	82
Figure 5.7	cyclic voltammetry for 1 mg/cm ² Pt/C _{HSA} cathode in 1 M KOH in with 1.5 M calcium hypochlorite mixed with oxygen saturated solution at 50 mV/s scan rate ; Temperature: 25 °C.	83
Figure 5.8a	Polarization and power density curves of MFC for 0.5 M glycerol mixed with 0.5 M KOH at anode and cathode electrolyte of 0.5 M KOH using (a) varying flow rate at anode and fixed flow rate 1 ml/min at cathode; Anode: Pd-Ni (10:10)/C of 1 mg/cm ² and cathode: Pt/C _{HSA} of 1 mg/cm ² , MFC temperature: 35 °C; Dotted line – power density curves; Solid lines – polarization curves.	84
Figure 5.8b	Polarization and power density curves of MFC for 0.5 M glycerol mixed with 0.5 M KOH at anode and cathode electrolyte of 0.5 M KOH using varying flow rate at cathode and optimum flow rate at anode (1 ml/min); Anode: Pd-Ni (10:10)/C of 1 mg/cm ² and cathode: Pt/C _{HSA} of 1 mg/cm ² , MFC temperature: 35 °C; Dotted line – power density curves; Solid lines – polarization curves.	85
Figure 5.9	Polarization and power density curves of MFC for the different types of anode electrocatalyst using anode fed of 0.5 M glycerol mixed with 0.5 M KOH and cathode electrolyte of 0.5 M KOH; Cathode: Pt/C _{HSA} of 1 mg/cm ² , MFC temperature: 35 °C ; Dotted line – power density curves; Solid lines – polarization curves.	87
Figure 5.10	Polarization and power density curves of MFC for different loading of anode electrocatalyst and fixed cathode loading of 1 mg/cm ² Pt/C _{HSA} using anode fed of 0.5 M glycerol mixed with 0.5 M KOH and cathode electrolyte of 0.5 M KOH; MFC temperature: 35 °C ; Dotted line – power density curves; Solid lines – polarization curves.	88
Figure 5.11	Polarization and power density curves of MFC for different loading of cathode electrocatalyst and anode loading of 1.5 mg/cm ² Pd-Ni (10:10)/C using anode fed of 0.5 M glycerol mixed with 0.5 M KOH and cathode electrolyte of 0.5 M KOH; MFC temperature: 35 °C ; Dotted line – power density curves; Solid lines – polarization curves.	90

Figure 5.12	Polarization and power density curves of MFC for different anode side KOH concentration mixed with 0.5 M glycerol at anode and cathode electrolyte of 0.5 M KOH; Anode: Pd-Ni (10:10)/C of 1.5 mg/cm ² and cathode: Pt/C _{HSA} of 1.5 mg/cm ² ; MFC temperature: 35 °C ; Dotted line – power density curves; Solid lines – polarization curves.	92
Figure 5.13	Polarization and power density curves of MFC for different cathode side KOH concentration and 0.5 M glycerol mixed with anode KOH electrolyte of 0.5 M KOH; Anode: Pd-Ni (10:10)/C of 1.5 mg/cm ² and cathode: Pt/C _{HSA} of 1.5 mg/cm ² ; MFC temperature: 35 °C ; Dotted line – power density curves; Solid lines – polarization curves.	93
Figure 5.14	Polarization and power density curves of MFC for different glycerol concentration mixed with 0.5 M KOH electrolyte at anode side and cathode electrolyte of 0.5 M KOH; Anode: Pd-Ni (10:10)/C of 1.5 mg/cm ² and cathode: Pt/C _{HSA} of 1.5 mg/cm ² ; MFC temperature: 35 °C ; Dotted line – power density curves; Solid lines – polarization curves.	95
Figure 5.15	Polarization and power density curves of MFC for different cell temperature with 0.5 M glycerol mixed with 0.5 M KOH electrolyte at anode and cathode electrolyte of 0.5 M KOH; Anode: Pd-Ni (10:10)/C of 1.5 mg/cm ² and cathode: Pt/C _{HSA} of 1.5 mg/cm ² ; MFC temperature: 35 °C ; Dotted line – power density curves; Solid lines – polarization curves.	96
Figure 5.16a	Polarization and power density curves of MFC for 1 M glycerol mixed with 1 M KOH at anode and cathode electrolyte of 0.5 M KOH using varying flow rate at anode and fixed flow rate at cathode of 1 ml/min; Anode: Pd-Ni (10:10)/C of 1 mg/cm ² and cathode: Pt/C _{HSA} of 1 mg/cm ² , MFC temperature: 35 °C; Dotted line – power density curves; Solid lines – polarization curves.	98
Figure 5.16b	Polarization and power density curves of MFC for 1 M glycerol mixed with 1 M KOH at anode and cathode electrolyte of 0.5 M KOH using varying flow rate at cathode and fixed flow rate at anode (1.2 ml/min); Anode: Pd-Ni (10:10)/C of 1 mg/cm ² and cathode: Pt/C _{HSA} of 1 mg/cm ² , MFC temperature: 35 °C; Dotted line – power density curves; Solid lines – polarization curves.	99
Figure 5.17	Polarization and power density curves from air breathing MFC for the different types of anode electrocatalyst using anode fed of 1 M glycerol mixed with 1 M KOH and cathode electrolyte of 0.5 M KOH with atmospheric air as oxidant; cathode: Pt/C _{HSA} of 1 mg/cm ² ; MFC temperature: 35 °C ; Dotted line – power density curves; Solid lines – polarization curves.	101
Figure 5.18	Polarization and power density curves from air breathing MFC for varying loading of anode electrocatalyst Pd-Ni (10:10)/C and fixed cathode loading of 1 mg/cm ² Pt/C _{HSA} using anode fed of 1 M glycerol mixed with 1 M KOH and cathode electrolyte of 0.5 M KOH with atmospheric air as oxidant; MFC temperature: 35 °C ; Dotted line – power density curves; Solid lines – polarization curves.	102
Figure 5.19	Polarization and power density curves from air breathing MFC for varying loading of cathode electrocatalyst and optimum anode loading of 1 mg/cm ² Pd-Ni (10:10)/C using anode fed of 1 M glycerol mixed with 1 M KOH and cathode fed of 0.5 M KOH electrolyte with atmospheric air as oxidant; MFC temperature: 35 °C; Dotted line – power density curves; Solid lines – polarization curves.	104

Figure 5.20	Polarization and power density curves from air breathing MFC for varying glycerol concentration mixed with 1 M KOH electrolyte at anode side and 0.5 M KOH electrolyte with atmospheric air as oxidant at cathode side. Anode electrocatalyst was optimum 1 mg/cm ² Pd-Ni (10:10)/C; Cathode electrocatalyst was optimum 1 mg/cm ² Pt/C _{HSA} ; MFC temperature: 35 °C; Solid lines – polarization curves; Dotted lines – power density curves.	105
Figure 5.21	Polarization and power density curves for varying concentration of KOH electrolyte at anode side mixed with optimum 1 M glycerol and 0.5 M KOH electrolyte with atmospheric air as oxidant at cathode side. Anode electrocatalyst was optimum 1 mg/cm ² Pd-Ni (10:10)/C; Cathode electrocatalyst was optimum 1 mg/cm ² Pt/C _{HSA} ; MFC temperature: 35 °C; Solid lines – polarization curves; Dotted lines – power density curves.	107
Figure 5.22	Polarization and power density curves for varying concentration of KOH electrolyte with atmospheric air as oxidant at cathode side and optimum 1 M glycerol and 1 M KOH electrolyte at anode side. The anode electrocatalyst was optimum loading 1 mg/cm ² of Pd-Ni(16:4)/C and cathode electrocatalyst was optimum loading 1 mg/cm ² of Pt/C _{HSA} for both cases; MFC temperature: 35 °C; Solid lines – polarization curves; Dotted lines – power density curves.	108
Figure 5.23	Polarization and power density curves of MFC for different cell temperature with 1 M glycerol mixed with 1 M KOH electrolyte at anode and cathode electrolyte of 1 M KOH; Anode: Pd-Ni (10:10)/C of 1 mg/cm ² and cathode: Pt/C _{HSA} of 1 mg/cm ² ; MFC temperature: 35 °C; Dotted line – power density curves; Solid lines – polarization curves.	110
Figure 5.24	Polarization and power density curves from air breathing MFC for varying concentrations of calcium hypochlorite and atmospheric air as mixed oxidant as catholyte and optimum 1 M glycerol mixed with 1 M KOH electrolyte as anolyte. The anode electrocatalyst was 1 mg/cm ² of Pd-Ni (10:10)/C and cathode electrocatalyst was 1 mg/cm ² of Pt/C _{HSA} . MFC temperature: 35 °C; Solid lines – polarization curves; Dotted lines – power density curves.	112
Figure 5.25	Comparison of polarization and power density curves for different types of hypochlorite with air as mixed oxidant and atmospheric air oxidant in air breathing MFC. Anolyte: 1 M glycerol mixed with optimum concentration of 1 M KOH; Catholyte: 1 M KOH. Pd-Ni (10:10)/C anode electrocatalyst of 1 mg/cm ² and Pt/C _{HSA} cathode electrocatalyst of 1 mg/cm ² . MFC temperature: 35°C. Solid line – polarization curves; Dotted line – power density curves.	114
Figure 5.26	XRD profile for the Pd-Pt/C of different weight ratios and Pd/C electrocatalyst.	16
Figure 5.27a	SEM/EDX image of synthesized Pd/C electrocatalyst.	119
Figure 5.27b	SEM/EDX image of synthesized Pd-Pt (16:4)/C electrocatalyst.	119
Figure 5.27c	SEM/EDX image of synthesized Pd-Pt (10:10)/C electrocatalyst.	119
Figure 5.27d	SEM/EDX image of synthesized Pd-Pt (4:16)/C electrocatalyst.	120

Figure 5.28a	TEM image and histogram of particles distribution of synthesized Pd/C electrocatalyst.	121
Figure 5.28b	TEM image and histogram of particles distribution for Pd-Pt (16:4)/C electrocatalyst.	122
Figure 5.28c	TEM image and histogram of particles distribution for Pd-Pt (10:10)/C electrocatalyst.	122
Figure 5.28d	TEM image and histogram of particles distribution for Pd-Pt (4:16)/C electrocatalyst.	122
Figure 29	Cyclic voltammetry for 1 M glycerol in 1 M KOH at scan rate of 50 mV/sec using Pd/C and different ratios of Pd-Pt/C as anode electrocatalyst; Temperature: 25 °C.	124
Figure 30a	Nyquist plots of synthesized electrocatalysts recorded at - 0.2 V in 1M glycerol mixed with 1M KOH solution; Temperature: 25 °C.	127
Figure 30b	Equivalent circuit diagram corresponds to Nyquist plot.	127
Figure 5.31	Polarization and power density curves of MFC for different types of anode electrocatalyst and fixed cathode electrocatalyst Pt/C _{HSA} with 2 mg/cm ² loading at both side, using 0.5 M glycerol and 0.5 M KOH at anode side and 0.5 M KOH at cathode side with ambient air as oxidant at a temperature of 35 °C. Solid line – polarization curves; Dotted line – power density curves.	128
Figure 5.32	Polarization and power density curves of MFC for different anode electrocatalyst loading of Pd-Pt (16:4)/C and cathode electrocatalyst loading 2 mg/cm ² of Pt/C _{HSA} , using 0.5 M glycerol and 0.5 M KOH at anode side and 0.5 M KOH with ambient air as oxidant at cathode side at a temperature of 35 °C. Solid line – polarization curves; Dotted line – power density curves.	130
Figure 5.33	Polarization and power density curves of MFC for different cathode electrocatalyst loading of Pt/C _{HSA} and cathode electrocatalyst loading of 2 mg/cm ² Pd-Pt/C, using 0.5 M glycerol and 0.5 M KOH at anode side and 0.5 M KOH with ambient air as oxidant at cathode side at a temperature of 35 °C. Solid line – polarization curves; Dotted line – power density curves.	131
Figure 5.34	Polarization and power density curves of MFC for different anode electrolyte concentration using 0.5 M glycerol at anode side and 0.5 M KOH with ambient air as oxidant at cathode side; Anode: Pd-Pt (16:4)/C of 2 mg/cm ² and cathode: Pt/C _{HSA} of 2 mg/cm ² ; MFC temperature: 35 °C. Solid line – polarization curves; Dotted line – power density curves.	133
Figure 5.35	Polarization and power density curves of MFC for different cathode KOH electrolyte concentration with ambient air as oxidant at cathode and 0.5 M glycerol mixed with 0.5 M KOH at anode side Anode: Pd-Pt (16:4)/C of 2 mg/cm ² and cathode: Pt/C _{HSA} of 2 mg/cm ² ; MFC temperature: 35 °C; Solid line – polarization curves; Dotted line – power density curves.	134
Figure 5.36	Polarization and power density curves of MFC for different fuel concentration with optimum electrolyte concentration of 0.5 M KOH at anode side and at cathode side 0.5 M KOH with ambient air as oxidant Anode: Pd-Pt (16:4)/C of 2 mg/cm ² and cathode: Pt/C _{HSA} of 2 mg/cm ² ; MFC temperature: 35 °C.; Solid line – polarization curves; Dotted line – power density curves.	136

Figure 5.37	Polarization and power density curves of MFC for different cell temperature with optimum fuel and electrolyte concentration of 0.5 M KOH at anode side and at cathode side 0.5 M KOH with ambient air as oxidant Anode: Pd-Pt (16:4)/C of 2 mg/cm ² and cathode: Pt/C _{HSA} of 2 mg/cm ² ; MFC temperature: 35 °C.; Solid line – polarization curves; Dotted line – power density curves.	137
Figure 5.38	Polarization and power density curves of MFC for the different types of anode electrocatalyst using anode fed of 1 M glycerol mixed with 1 M KOH and cathode electrolyte of 0.5 M KOH; MFC temperature: 35 °C ; Dotted line – power density curves; Solid lines – polarization curves.	139
Figure 5.39	Polarization and power density curves of MFC for different loading of anode electrocatalyst and fixed cathode loading of 1 mg/cm ² Pt/C _{HSA} using anode fed of 1 M glycerol mixed with 1 M KOH and cathode electrolyte of 0.5 M KOH; MFC temperature: 35 °C; Dotted line – power density curves; Solid lines – polarization curves.	140
Figure 5.40	Polarization and power density curves of MFC for different loading of cathode electrocatalyst and fixed anode loading of 1 mg/cm ² Pd-Pt (16:4)/C using anode fed of 1 M glycerol mixed with 1 M KOH and cathode electrolyte of 0.5 M KOH; MFC temperature: 35 °C ; Dotted line – power density curves; Solid lines – polarization curves.	142
Figure 5.41	Polarization and power density curves of MFC for anode fed glycerol of different concentration mixed with 1 M KOH and cathode electrolyte of 0.5 M KOH; Anode: Pd-Pt (16:4)/C of 1 mg/cm ² and cathode: Pt/C _{HSA} of 1 mg/cm ² ; MFC temperature: 35 °C ; Dotted line – power density curves; Solid lines – polarization curves.	144
Figure 5.42	Polarization and power density curves of MFC for different KOH concentration mixed with 1 M glycerol at anode and fixed cathode electrolyte of 0.5 M KOH; Anode: Pd-Pt (16:4)/C of 1 mg/cm ² and cathode: Pt/C _{HSA} of 1 mg/cm ² ; MFC temperature: 35 °C; Dotted line – power density curves; Solid lines – polarization curves.	145
Figure 5.43	Polarization and power density curves of MFC for different cathode KOH electrolyte concentration and 1 M glycerol mixed with 1.5 M KOH at anode side. Anode: Pd-Pt (16:4)/C of 1 mg/cm ² and cathode: Pt/C _{HSA} of 1 mg/cm ² ; MFC temperature: 35 °C; Dotted line – power density curves; Solid lines – polarization curves.	146
Figure 5.44	Polarization and power density curves of MFC at different temperatures and anode fed of 1 M glycerol mixed with 1.5 M KOH, and cathode electrolyte of 0.5 M KOH; Anode: Pd-Pt (16:4)/C of 1 mg/cm ² and cathode: Pt/C _{HSA} of 1 mg/cm ² , Dotted line – power density curves; Solid lines – polarization curves.	148
Figure 5.45	Polarization and power density curves from MFC for varying concentrations of calcium hypochlorite and atmospheric air as mixed oxidant as catholyte and optimum 1 M glycerol mixed with 1.5 M KOH electrolyte as anolyte; Anode: 1 mg/cm ² of Pd-Pt (16:4)/C; Cathode: 1 mg/cm ² of Pt/C _{HSA} ; Solid line – polarization curves; Dotted line – power density curves.	150
Figure 5.46	Actual versus model predicted power density comparison.	159

Figure 5.47	Predicted vs. Residual value of power density obtains from air breathing T-shaped MFC.	160
Figure 5.48a	Polarization and power density curves for optimum condition of 1.07 M glycerol fuel mixed with 1.62 M KOH as electrolyte, anode electrocatalyst loading of 1.12 mg/cm ² and cathode electrolyte of 0.69 M KOH, Solid line -polarization curves; Dotted line- power density curves.	161
Figure 5.48b	Polarization and power density curves of MFC for random condtion of 1 M glycerol fuel mixed with 1 M KOH as electrolyte, anode electrocatalyst loading of 1 mg/cm ² and cathode electrolyte of 1 M KOH; Solid line – polarization curves; Dotted line – power density curves.	163
Figure 5.49a	Response surface 3D plot showing the effect of glycerol concentration (A) and anode electrolyte concentration (B).	165
Figure 5.49b	Response surface 3D plot showing the effect of glycerol concentration (A) and anode electrocatalyst loading (C).	165
Figure 5.49c	Response surface 3D plot showing the effect of anode electrolyte concentration (B) and anode electrocatalyst loading (C).	166
Figure 5.49d	Response surface 3D plot showing the effect of glycerol concentration (A) and cathode electrolyte concentration (D).	166
Figure 5.49e	Response surface 3D plot showing the effect of anode electrolyte concentration (B) and cathode electrolyte concentration (D).	167
Figure 5.49f	Response surface 3D plot showing the effect of anode electrocatalyst loading (C) and cathode electrolyte concentration (D).	167
Figure 5.50	Perturbation plot displaying the effect independent variables on power density.	170
Figure 5.51	Stability test of the Y-shaped and T-shaped air breathing MFC using the optium conditions of operation at constant load at a temperature of 35 °C.	181

LIST OF TABLES

Table 2.1	Performance comparison of different electrocatalyst for glycerol electrooxidation in half cell study.	31
Table 2.2	Performance comparison of different electrocatalyst for glycerol fuel in microfluidic fuel cell.	44
Table 3.1	Properties of glycerol fuel (Fisher scientific, India).	47
Table 3.2	Properties of Toray Carbon paper, TGP-H-60 (Alfa Aesar, USA).	47
Table 3.3	Composition and properties of Nafion [®] solution (Alfa Aesar, USA).	48
Table 3.4	Properties of PTFE Dispersion (Sigma Aldrich, USA).	48
Table 4.1	Full factorial four factor level for RSM study.	67
Table 5.1	Crystallite size and peak position of Pd-Ni/C electrocatalyst obtained from XRD data.	71
Table 5.2	Composition of electrocatalyst weight percentage obtained from EDX.	74
Table 5.3	Equivalent circuit related terms for Pd-Ni/C electrocatalysts.	80
Table 5.4	Physical parameters derived from XRD data of the plane (111) for Pd/C and Pd-Pt/C bimetallic electrocatalyst	117
Table 5.5	Surface concentration of metal in synthesized electrocatalyst with different weight ratios.	120
Table 5.6	Equivalent circuit related terms for Pd/C and Pd-Pt/C electrocatalysts.	127
Table 5.7	Comparison of Pd-Pt (16:4)/C anode electrocatalyst in Y-shaped and T-shaped air breathing MFC at optimum MFC conditions and at room temperature.	151
Table 5.8	Comparison of Pd-Ni (10:10)/C anode electrocatalyst in Y-shaped and T-shaped air breathing MFC at optimum MFC conditions and at room temperature.	152
Table 5.9	BBD arrangements and response for glycerol electrooxidation regarding power density.	155
Table 5.10	Model summary statistics.	156
Table 5.11	ANOVA for Response Surface Quadratic Model.	157
Table 5.12	Comparison of predicted and actual power density at the optimum condition obtained from the model.	162

Table 5.13	Comparison of predicted and actual/experimental power density at the random condition of MFC.	163
Table 5.14	Reynolds numbers for different flow rates in Y-shaped MFC.	172
Table 5.15	Peclet numbers for different flow rates in Y-shaped MFC.	173
Table 5.16	Reynolds numbers for different flow rates in T-shaped MFC.	174
Table 5.17	Peclet numbers for different flow rates in T-shaped MFC.	175
Table 5.18	Performance comparison of present study with published work.	178
Table 5.19	Efficiency of Y-shaped and T-shaped MFC using best Pd-Pt/C and Pd-Ni/C anode electrocatalysts at room temperature (35 °C) and atmospheric pressure (1 atm).	180

NOMENCLATURE

Alphabetic symbols	Meaning
A	Glycerol concentration
a	lattice parameter
B	Anode electrolyte concentration
C	Anode electrocatalyst loading
C _{AB}	Acetylene black carbon
C _p	Central points
D	Cathode electrolyte concentration
d _c	average crystallite size
d _{hkl}	interplanar distance between two planes of Miller index (hkl)
d _h	Hydraulic diameter
2FI	Two factor interaction
F	Faraday's constant
k	number of factors in RSM study
N	Total number of experiments in RSM study
p-value	Probability value
R	universal gas constant
R ²	Coefficient of determination
T	operating temperature
x _i and x _j	Independent variables for the studied factor
Y	Predicted response
z	Downstream length
Abbreviations	Meaning
ANOVA	Analysis of variance
AFC	Alkaline fuel cell
BBD	Box-Behnken Design
CEA	Central electricity authority
CV	Cyclic Voltammetry
3D	Three-dimensional
DF	Degree of freedom
EDX	Energy dispersive X-ray spectroscopy

SEM	Scanning Electron Microscopy
GDL	Gas Diffusion Layer
LFFC	Laminar flow fuel cell
MWCNT	Multi-walled carbon nanotube
MCFC	Molten Carbonate Fuel Cell
MFC	Microfluidic fuel cell
OCV	Open circuit voltage
ORR	Oxygen Reduction Reaction
PEMFC	Proton Exchange Membrane Fuel Cell
PAFC	Phosphoric Acid Fuel Cell
PRESS	Predicted residual error sum of squares
RSM	Response surface methodology
SOFC	Solid Oxide Fuel Cell
TEM	Transmission Electron Microscopy
XRD	X-Ray Diffraction

Greek Symbols**Meaning**

α_a	Anodic charge transfer co-efficient
α_b	Cathodic charge transfer co-efficient
β_o	Linear parameter
β_{ii}	Quadratic parameter
β_{ij}	Interaction parameter
μ	Viscosity
β	width of the peak (in radians) at its half-height
κ	Scherrer constant (0.90 for spherical crystallite)
λ	X-ray wavelength used (1.54056 Å for Cu-K _{α1} radiation)
ρ	Density
\vec{u}	Velocity field
δ_x	Broadening width
η	surface overpotential

PREFACE

In the present world scenario, limited resources of fossil fuels with high demand are the major cause for researchers to develop environment friendly power generating devices. The fuel cell device produces energy without any toxic emissions to the environment. Microfluidic fuel cells (MFCs) are one of the most recently developed and investigated micro fuel cell device which has created interest among the researchers these days for further studies due to its possible potential uses in portable electrical and electronic devices. In MFC, the electrodes are fixed in a microchannel with a distance between electrodes of less than 1 mm without having any solid membrane electrolyte. The anode and cathode streams are maintained in laminar flow and with a low Reynolds number. Recently, a new type of microfluidic fuel cell was developed by Jayashree et al., (2005) known as air breathing microfluidic fuel cell consisting air breathing cathode. There are several advantages of using air breathing cathode in MFC e.g., cathode electrocatalysts sites get exposed to the higher concentration of oxygen via air breathing cathode in comparison to that of oxygen dissolved in aqueous solution due to low solubility of oxygen. Thus, in the present study Y-shaped and T-shaped air breathing microfluidic fuel cell was fabricated for experimental studies and validation of developed model equation through Response surface methodology (RSM). Glycerol fuel has comparable energy density to that of methanol and ethanol and it is a byproduct of biodiesel manufacturing via transesterification of vegetable oils and readily available. It is non-toxic, non-flammable, non-volatile and having high boiling point (290 °C). Thus, glycerol was selected as most promising fuel for the present study in a specially design MFC. The anode electrocatalyst of different metal compositions of Pd-Pt/C and Pd-Ni/C were synthesized to improve the electrooxidation kinetics and activity via a suitable reaction

pathway which allows to split the C-C bond of glycerol at low activation energy. whereas, commercial Pt (40 wt.%)/C_{HSA} was used as cathode electrocatalyst.

The Y-shaped and T-shaped air breathing MFC were fabricated from perspex sheet (PMMA) using CNC milling machine. Potassium hydroxide (KOH) was used as electrolyte. The acetylene black supported anode electrocatalyst was synthesized using PdCl₂, H₂PtCl₆. 6H₂O and NiCl₂.6H₂O precursors by impregnation reduction method. The synthesized bimetallic anode electrocatalyst were Pd/C, Pd-Pt (16:4)/C, Pd-Pt (10:10)/C, Pd-Pt (4:16)/C, Pd-Ni (16:4)/C, Pd-Ni (10:10)/C and Pd-Ni (4:16)/C. The prepared electrocatalysts were analysed by X-ray Diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray (EDX) and transmission electron microscopy (TEM) for physical characterization. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed for electrochemical characterizations of the synthesized anode electrocatalysts. The cathode electrocatalyst was commercial Pt (40 wt. %)/C_{HSA}. The Toray carbon paper (TGP-H-60) was used for electrode preparation. The ink was made by adding required quantity of electrocatalyst, isopropanol, Nafion[®] dispersion (D-520, 5 wt. %) and PTFE dispersion (60 wt. %). The prepared ink was painted with the help of paintbrush on carbon paper for anode and cathode preparation.

The experiment was performed using synthesized anode electrocatalysts for both type of MFC to obtain maximum cell performance. The electrode area was 0.6 cm² (3 cm × 0.2 cm) and 0.9 cm² (3 cm × 0.3 cm) for Y-shaped MFC and T-shaped MFC, respectively. Important cell parameters such as flow rate, glycerol concentration, electrolyte concentration, anode electrocatalyst type, anode electrocatalyst loading, cathode electrocatalyst loading, oxidant type and cell temperature were thoroughly and systematically studied in fabricated MFC. Further, the optimization study using response surface methodology in MFC was performed. The dimensionless numbers and cell

efficiency were evaluated for both type of MFC. Finally the stability test were performed for both type of MFC using best anode electrocatalyst.

The performance of anode electrocatalyst Pd-Pt/C and Pd-Ni/C of different compositions were evaluated in both Y-shaped and T-shaped air breathing MFC. The synthesized electrocatalyst Pd-Pt (16:4)/C shows better performance than other ratios in half cell and single cell studies. Similarly, Pd-Ni (10:10)/C shows better performance than other ratios in half cell and single cell studies. However, Pd-Pt (16:4)/C exhibited better performance than the Pd-Ni (10:10)/C electrocatalyst in both type i.e., Y-shaped and T-shaped design, respectively. The Pd-Pt (16:4)/C in Y-shaped MFC at optimum cell conditions i.e., flow rate of anode and cathode streams of 1 ml/min, glycerol concentration 0.5 M, electrolyte/KOH concentration of 0.5 M at anode and 0.5 M at cathode, electrocatalyst loading at anode 2 mg/cm² and cathode 2 mg/cm², and cell temperature of 75 °C produced highest OCV of 0.93 V and maximum power density of 2.11 mW/cm² at a current density of 5.14 mA/cm². The same electrocatalyst Pd-Pt (16:4)/C in T-shaped produced little lower OCV of 0.78 V and maximum power density of 4.03 mW/cm² at the optimum cell conditions i.e., flow rate of 1.2 ml/min at anode and 1 ml/min at cathode, glycerol concentration 1 M, electrolyte/KOH concentration of 1.5 M at anode and 0.5 M at cathode, electrocatalyst loading at anode 1 mg/cm² and cathode 1 mg/cm², and cell temperature of 75 °C.

The Pd-Ni (10:10)/C in Y-shaped MFC at optimum cell conditions i.e., flow rate of anode and cathode streams of 1 ml/min, glycerol concentration 0.5 M, electrolyte/KOH concentration of 0.5 M at anode and 0.5 M at cathode, electrocatalyst loading at anode 1.5 mg/cm² and cathode 1.5 mg/cm², and cell temperature of 75 °C produced highest OCV of 0.8 V and maximum power density of 1.6 mW/cm² at a current density of 4.41 mA/cm². The same electrocatalyst Pd-Ni (10:10)/C in T-shaped produced little lower OCV of 0.51

V and maximum power density of 2.14 mW/cm^2 at the optimum cell conditions i.e., flow rate of 1.2 ml/min at anode and 1 ml/min at cathode, glycerol concentration 1 M, electrolyte/KOH concentration of 1 M at anode and 1 M at cathode, electrocatalyst loading at anode 1 mg/cm^2 and cathode 1 mg/cm^2 , and cell temperature of $75 \text{ }^\circ\text{C}$.

After, optimization of process parameters using RSM, the predicted maximum power density was 2.79 mW/cm^2 at the optimum condition and the actual/experimental power density obtained was 2.76 mW/cm^2 . The RSM study indicates that cathode side KOH concentration has the least effect on cell performance. The stability test shows that the performance decreases with time due to poisoning of the electrode surface.

The subject matter contained in the thesis has been arranged in six different chapters. **Chapter I** is Introduction of thesis. Literature review and objectives are presented in **Chapter II**. **Chapter III** is Experimental which describes about material used and then experimental setups and methods. Process optimization by RSM is discussed in the **Chapter IV**. Results and Discussion are thoroughly represented in Chapter V. Finally, the conclusions of thesis is presented in **Chapter VI**.