EXPERIMENTAL AND COMPUTATIONAL STUDY OF AN AIR-BREATHING MICRO LIQUID FUEL CELL WITH AN EXTENDED ACTIVE ANODE CATALYST REGION

by

Yinghui Zhang

B.Eng, China University of Petroleum, Beijing, 2009

M.Sc., China University of Petroleum, Beijing, 2012

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

in

THE FACULTY OF GRADUATE AND POSTDOCTORAL STUDIES

(Chemical and Biological Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA

(Vancouver)

June 2018

© Yinghui Zhang, 2018

The following individuals certify that they have read, and recommend to the Faculty of Graduate and Postdoctoral Studies for acceptance, the dissertation entitled:

Experimental and computational study of an air-breathing micro-direct liquid fuel cell with an extended active anode catalyst region

submitted by	Yinghui Zhang	in partial fulfillment of the requirements for
the degree of	Doctor of Philosophy	
in	Chemical and Biological Engineering	

Examining Committee:

Dr. Fariborz Taghipour

Co-supervisor

Dr. David P. Wilkinson

Co-supervisor

Dr. John Madden

Supervisory Committee Member

Dr. Vikramaditya G. Yadav

Supervisory Committee Member

Dr. James Feng

University Examiner

Dr. Edouard Asselin

University Examiner

Abstract

Portable electronic devices for the next generation demand a quick charging and longlasting energy power system. Micro direct methanol fuel cells (µDMFCs) are considered as one of the appropriate alternatives to rechargeable battery technology for portable power devices. Although a significant amount of work has been done with µDMFCs, it is still a design challenge to miniaturize the fuel cell and to provide adequate power.

The conventional bipolar fuel cell architecture contains a membrane electrode assembly sandwiched between two flow field plates. In this research, we present an approach to enhance the maximum power density of μ DMFCs without affecting the total fuel cell volume by depositing extra anode catalyst on the fuel flow channel walls.

An air-breathing µDMFC with extra anode catalyst deposited on the channel walls was developed, and the effects of key design parameters and operating conditions on the fuel cell performance were examined by measuring the overall cell and individual electrode polarization curves. The fuel cell with extra anode catalyst on the channel walls improved the maximum power density by 20% compared to the conventional design with only a catalyst coated membrane.

The fuel cell design approach with catalyzed flow field channel walls was also demonstrated in an air-breathing micro Fe(II)/Fe(III) redox anode fuel cell (μ RAFC). The μ RAFC with graphite channel walls as an anode improved the maximum power density

iii

by 281% compared to the μ RAFC with inactive channel walls. The impacts of key operating conditions on the cell performance were also evaluated.

A 3D simplified model for the µDMFC design with catalyzed channel walls was developed and applied to evaluate the key parameters. It was found that the fuel cell performance was mainly limited by the kinetics of the methanol oxidation reaction. For the fuel cell with anode catalyst both on the membrane and the channel walls, increasing the anode catalyst loading on the channel walls improved the contribution of the anode on the wall to the total anodic current, and reducing the channel dimensions only slightly improved the cell performance.

Lay Summary

A micro direct methanol fuel cell (μ DMFC) is a device that generates electrical power by the reaction of methanol and oxygen. μ DMFC is considered as one of the promising alternatives to the rechargeable battery for portable power devices. However, it is still a design challenge to miniaturize the fuel cell and to provide adequate power. For a typical μ DMFC design, the catalyst layer where the reaction occurs is only on a membrane. In this research, we developed a μ DMFC with extra anode catalyst on the fuel flow channel walls. The maximum power density of the fuel cell was improved due to the increased anode reaction rate compared to the conventional design. This design approach with extra anode catalyst coated on the channel walls is a feasible way to enhance the maximum power density of the conventional fuel cell but without impacting the dimensions of the micro fuel cell.

Preface

All the experimental and modeling data presented in this thesis were obtained by the author, under the supervision of Professors Fariborz Taghipour and David P. Wilkinson at the University of British Columbia (UBC). Most of the experimental work was conducted in the Applied Electrochemist & Fuel Cell Lab at the Department of Chemical and Biological Engineering, the University of British Columbia.

All of the research, including the establishment of objectives, design, and development of the fuel cell, experimental design and implementation, model development, data analysis, and thesis writing were completed by the author with valuable guidance from Professors Fariborz Taghipour and David P. Wilkinson.

The fuel cell design concept in Chapter 2 and some preliminary results were presented at the International Conference on Electrochemical Energy Science and Technology (EEST2015) in Vancouver, Canada, on Aug. 16-22, 2015.

All the materials presented in this thesis have not yet been published and three manuscripts of the work presented in Chapter 2-4 are in preparation for submission in peer-reviewed journals under the guidance of Professors Fariborz Taghipour and David P. Wilkinson.

Table of Contents

Abstractiii
Lay Summaryv
Preface vi
Table of Contents vii
List of Tables xii
List of Figures xiv
List of Symbolsxxiii
List of Abbreviationsxxvi
Acknowledgmentsxxvii
Dedicationxxviii
Chapter 1: Introduction1
1.1 A brief background of fuel cell technology1
1.2 Basic principles of fuel cell design5
1.2.1 Thermodynamics of the fuel cell5
1.2.1.1 Standard cell and electrode potentials5
1.2.1.2 The effect of concentration7
1.2.1.3 The effect of temperature
1.2.1.4 The effect of pressure9
1.2.1.5 Thermodynamic efficiency9
1.2.2 Fuel cell irreversibilities10
1.2.3 Activation losses 11
1.2.4 Ohmic losses

1.2.4.1 Liquid electrolyte1	3
1.2.4.2 Solid electrolyte: Ion exchange membrane1	5
1.2.5 Mass Transport losses1	5
1.2.6 Fuel crossover losses	6
1.2.7 Efficiency of the fuel cell1	6
1.3 The direct methanol fuel cell	7
1.3.1 Micro DMFC architectures	1
1.3.2 Catalyst loading process2	7
1.3.2.1 Catalyst loading methods2	7
1.3.2.2 Anode catalyst loading amount2	7
1.3.3 Operating conditions of µDMFCs2	8
1.3.3.1 Methanol concentration effect20	8
1.3.3.2 Air-breathing cathode2	9
1.4 The redox flow battery	0
1.5 The redox fuel cell	2
1.6 Knowledge gap	4
1.7 Research objectives	6
1.8 Thesis layout	7
Chapter 2: Micro direct methanol fuel cell with a catalyzed flow field channel 3	9
2.1 Introduction	9
2.2 Experimental	9
2.2.1 Electrode preparation and fuel cell assembly	9
2.2.2 Fuel cell performance characterization4	3

2	.2.3	Design parameters	43
2	.2.4	Operating conditions	44
2.3	Res	sults and discussion	46
2	.3.1	Design parameters	46
	2.3.1.	1 Anode catalyst distribution	47
	2.3.1.	2 Anode catalyst loading on the channel walls	51
2	.3.2	Operating conditions	53
	2.3.2.	1 Effect of methanol concentration	54
	2.3.2.	2 Effect of anode flow rate	58
	2.3.2.	3 Effect of sulfuric acid concentration	62
	2.3.2.	4 Effect of air supply mode	68
2.4	Sur	nmary	71
Chap	ter 3: I	Micro redox anode fuel cell with catalyzed flow field channel	72
3.1	Intr	oduction	72
3.2	Exp	perimental	73
3	.2.1	Electrode preparation and cell assembly	73
3	.2.2	µRAFC performance characterization	75
3	.2.3	Experimental design and operating conditions	76
3.3	Res	sults and discussion	77
3	.3.1	Design parameters	77
	3.3.1.	1 Anode distribution	77
	3.3.1.	2 Thickness of the anode on the membrane	80
3	.3.2	Operating conditions	83

	3.3.2.′	1 Anolyte flow rate	83
	3.3.2.2	2 Effect of sulfuric acid concentration	85
3.4	Sum	nmary	88
Chapte	er 4: N	Modeling of micro direct methanol fuel cells with catalyzed flow	<i>w</i> field
chann	el wal	ls	89
4.1	Intro	oduction	89
4.2	Мос	del equations	91
4.2	2.1	Proton and electron conservation equations	92
4.2	2.2	Electrochemical reaction models	94
4.2	2.3	Fluid flow models	96
4.2	2.4	Mass transport models	97
4.2	2.5	Boundary conditions	98
4.3	Con	nparison with experimental data	100
4.4	Мос	del application for evaluating important parameters	106
4.4	4.1	Effect of anode catalyst loading on the channel walls	107
4.4	4.2	Effect of anode catalyst distribution	113
4.4	4.3	Effect of ionic conductivity of liquid phase	116
4.4	4.4	Effect of ionic conductivity of solid phase conductor	120
4.4	4.5	Effect of channel geometry	125
4.5	Sun	nmary	131
Chapter 5: Conclusions and recommendations 133			
5.1	Con	clusions	133
5.1	1.1	Micro direct methanol fuel cell with catalyzed flow field channel walls	s 133

5	5.1.2	Micro redox anode fuel cell with catalyzed flow field channel walls 1	36
5	5.1.3	Modeling of micro direct methanol fuel cells with catalyzed flow field	eld
С	hanne	I walls1	38
5.2	Re	commendations1	40
Biblic	Bibliography144		
Appendices158			
Арр	oendix	A: Dimensioned drawings of the fuel cell components1	58
Арр	oendix	B: SEM photo of the catalyst coated membrane 1	63
Арр	pendix	C: Electrochemical impedance spectra1	64
C	C.1 I	mpedance spectra of the DMFC1	64
C	C.2 I	mpedance spectra of the µRAFC1	69
Арр	pendix	D: The membrane conductivity measurement1	72

List of Tables

Table 1.1 Comparison of fuel cell technologies
Table 1.2 Micro-Direct methanol fuel cells developed by different companies
Table 1.3 Half-cell potentials of basic redox couples
Table 2.1 Catalyst loadings of three different designs
Table 2.2 Operating conditions for the baseline case
Table 2.3 Operating conditions for the fuel cell designs (b) and (c)
Table 2.4 Cell resistances for μ DMFCs with different anode catalyst distributions 49
Table 2.5 Cell resistances and voltage losses for μ DMFCs with different anode catalyst
loadings on the channel walls
Table 2.6 Cell resistances and voltage losses for μ DMFCs with anode catalyst both on
the membrane and the channel walls under different sulfuric acid concentrations 63
Table 2.7 Cell resistances and voltage losses for $\mu DMFCs$ with anode catalyst only on
the membrane under different sulfuric acid concentrations
Table 2.8 Measured E_a at the OCV and calculated $E_{e,a}$ under different sulfuric acid
concentrations
Table 2.9 Cell resistances for μ DMFCs with different air supply modes
Table 3.1 Cell resistances at the OCV and voltage losses at 5 mA/cm ² for μ RAFCs with
different channel materials79
Table 3.2 Cell resistances for μ DMFCs with different anode catalyst loadings on the
walls
Table 4.1 Geometrical parameters for the 3D model. 91
Table 4.2 Parameters used in the model

Table 4.3 Anode catalyst loadings for fuel cells with different anode catalyst distributions.

List of Figures

Figure 1.1 Grove's gas voltaic battery2
Figure 1.2 Polarization curve for a fuel cell operated at low-temperature
Figure 1.3 Operation principles of the direct methanol fuel cell
Figure 1.4 Two basic designs of µDMFCs (a) bipolar, (b) planar
Figure 1.5 Schematic of a silicon-based planar micro direct methanol fuel cell: (a) top-
view (b) cross-sectional view of the design23
Figure 1.6 Schematic of a design of laminar flow fuel cell
Figure 1.7 Schematic and operating principles of a redox flow battery
Figure 2.1 (a) Schematic diagram of the different layers of the designed fuel cell; (b)
photos of different fuel cell components41
Figure 2.2 (a) Schematic diagram of the micro direct liquid fuel cell testing system; (b)
photo of the fuel cell setup
Figure 2.3 Cross-sectional view of designs with different anode catalyst distributions 44
Figure 2.3 Cross-sectional view of designs with different anode catalyst distributions 44 Figure 2.4 Polarization and power density curves for µDMFCs with different anode
Figure 2.3 Cross-sectional view of designs with different anode catalyst distributions 44 Figure 2.4 Polarization and power density curves for µDMFCs with different anode catalyst distributions at ambient temperature and pressure and 1 M methanol/0.1 M
Figure 2.3 Cross-sectional view of designs with different anode catalyst distributions 44 Figure 2.4 Polarization and power density curves for µDMFCs with different anode catalyst distributions at ambient temperature and pressure and 1 M methanol/0.1 M sulfuric acid at a flow rate of 0.1 ml/min
Figure 2.3 Cross-sectional view of designs with different anode catalyst distributions 44 Figure 2.4 Polarization and power density curves for µDMFCs with different anode catalyst distributions at ambient temperature and pressure and 1 M methanol/0.1 M sulfuric acid at a flow rate of 0.1 ml/min
Figure 2.3 Cross-sectional view of designs with different anode catalyst distributions44 Figure 2.4 Polarization and power density curves for µDMFCs with different anode catalyst distributions at ambient temperature and pressure and 1 M methanol/0.1 M sulfuric acid at a flow rate of 0.1 ml/min
Figure 2.3 Cross-sectional view of designs with different anode catalyst distributions 44 Figure 2.4 Polarization and power density curves for µDMFCs with different anode catalyst distributions at ambient temperature and pressure and 1 M methanol/0.1 M sulfuric acid at a flow rate of 0.1 ml/min
Figure 2.3 Cross-sectional view of designs with different anode catalyst distributions44 Figure 2.4 Polarization and power density curves for µDMFCs with different anode catalyst distributions at ambient temperature and pressure and 1 M methanol/0.1 M sulfuric acid at a flow rate of 0.1 ml/min
Figure 2.3 Cross-sectional view of designs with different anode catalyst distributions44 Figure 2.4 Polarization and power density curves for µDMFCs with different anode catalyst distributions at ambient temperature and pressure and 1 M methanol/0.1 M sulfuric acid at a flow rate of 0.1 ml/min

 Figure 2.14 Individual electrode polarization curves for µDMFCs with anode catalyst deposited both on the membrane and channel walls at different flow rates of 1 M methanol/0.1 M sulfuric acid solution......60 Figure 2.15 Individual electrode polarization curves for µDMFCs with anode catalyst deposited on the membrane only at different flow rates of 1 M methanol/0.1 M sulfuric acid solution......61 Figure 2.16 Polarization and power density curves for µDMFCs with anode catalyst deposited both on the membrane and channel walls at ambient temperature and pressure and different concentrations of sulfuric acid/1 M methanol at a flow rate of 0.2 Figure 2.17 Polarization and power density curves for µDMFCs with anode catalyst deposited on the membrane only at ambient temperature and pressure and different concentrations of sulfuric acid/1 M methanol at a flow rate of 0.2 ml/min......65 Figure 2.18 Individual electrode polarization curves for µDMFCs with anode catalyst deposited both on the membrane and channel walls under different sulfuric acid Figure 2.19 Individual electrode polarization curves for µDMFCs with anode catalyst Figure 2.20 Polarization curves for µDMFCs with anode catalyst deposited both on the membrane and channel walls under different air supply modes at ambient temperature Figure 2.21 Individual electrode polarization curves for µDMFCs with anode catalyst deposited both on the membrane and channel walls under different air supply modes.70

xvi

Figure 3.2 The polarization and power density curves for µRAFCs with different channel materials at ambient temperature and pressure and 1 M FeSO₄/1 M H₂SO₄ at a flow rate of 0.1 ml/min......78 Figure 3.3 Individual electrode polarization curves for µRAFCs with different channel materials at ambient temperature and pressure and 1 M FeSO₄/1 M H₂SO₄ at a flow rate of 0.1 ml/min......79 Figure 3.4 The polarization and power density curves for µRAFCs with a graphite channel and different layers of carbon paper at ambient temperature and pressure and 1 M FeSO₄/1 M H₂SO₄ at a flow rate of 0.1 ml/min.81 Figure 3.5 Individual polarization curves for µRAFCs with a graphite channel and different layers of carbon paper at ambient temperature and pressure and 1 M FeSO₄/1 M H₂SO₄ at a flow rate of 0.1 ml/min......82 Figure 3.6 The polarization and power density curves for µRAFCs with a graphite channel at ambient temperature and pressure and 1 M FeSO₄/1 M H₂SO₄ at different Figure 3.7 Individual electrode polarization curves for µRAFCs with a graphite channel Figure 3.8 The polarization and power density curves for µRAFCs with a graphite channel for different sulfuric acid concentrations/1 M FeSO₄ solution at a flow rate of 0.1

Figure 3.9 Individual electrode polarization curves for μ RAFCs with a graphite channel for different sulfuric acid concentrations/1 M FeSO₄ solution at a flow rate of 0.1 ml/min.

Figure 4.1 The modeled geometry of the fuel cell with anode catalyst deposited both on the membrane and the channel walls......90 Figure 4.2 Schematic illustration of the modeled phenomena and the potential boundary conditions in the micro-DMFC with anode catalyst deposited both on the membrane and Figure 4.3 Comparison of modeling and experimental polarization curves for µDMFCs with different anode catalyst distributions at ambient temperature and pressure and 1 M Figure 4.4 Comparison of modeling and experimental individual electrode polarization Figure 4.5 Methanol crossover fluxes at the interface of the membrane and cathode for Figure 4.6 Modeling results of the effect of anode catalyst loading on the channel walls on the performance of the µDMFCs with anode catalyst deposited both on the channel walls and membrane at ambient temperature and pressure and 1 M methanol/0.1 M sulfuric acid at a flow rate of 0.1 ml/min. CCM anode loading constant at 0.44 mg/cm². Figure 4.7 Modeling results of individual electrode performance for the µDMFCs of

Figure 4.6 with anode catalyst deposited both on the membrane and channel walls.. 108

Figure 4.8 Ionic potential losses in the acidic solution for different anode catalyst
loadings on the channel walls for μ DMFCs with anode catalyst deposited both on the
membrane and channel walls109
Figure 4.9 Current density generated from the catalyzed wall for different anode catalyst
loadings on the channel walls of μ DMFCs with anode catalyst deposited both on the
membrane and channel. i_{wall} is based on the geometrical area of the channel walls (0.9
cm ²)
Figure 4.10 Methanol crossover flux at the interface of the membrane and cathode for
different anode catalyst loadings on the channel walls of µDMFCs with anode catalyst
deposited both on the membrane and channel walls 111
Figure 4.11 Modeling results of the effect of anode catalyst loading on the channel walls
on the performance of μ DMFCs with anode catalyst deposited only on the channel walls
at ambient temperature and pressure and 1 M methanol/0.1 M sulfuric acid at a flow
rate of 0.1 ml/min112
Figure 4.12 Modeling results of the effect of anode catalyst loading on the channel walls
on the individual electrode performance for µDMFCs of Figure 4.11 with anode catalyst
deposited only on the channel walls112
Figure 4.13 Modeling results of the effect of anode catalyst distribution on the
performance of µDMFCs with the same total anode catalyst amount at ambient
temperature and pressure and 1 M methanol/0.1 M sulfuric acid at a flow rate of 0.1
ml/min

Figure 4.14 Modeling results of the effect of anode catalyst distribution on the individual electrode performance for µDMFCs of Figure 4.13 with the same total anode catalyst Figure 4.15 The modeled effect of the anode catalyst distribution on the average methanol concentration at the anode catalyst layer of µDMFCs with the same total Figure 4.16 The modeled effect of the acidic solution conductivity on the performance of µDMFCs with anode catalyst deposited both on the membrane and channel walls at ambient temperature and pressure and 1 M methanol at a flow rate of 0.1 ml/min..... 117 Figure 4.17 The modeled effect of the acidic solution conductivity on the individual electrode performance for the µDMFCs of Figure 4.16 with different concentrations of Figure 4.18 Modeling results of the current density generated from the catalyzed wall for different conductivities of acidic solutions for the µDMFCs of Figure 4.16. i_{wall} is based Figure 4.19 Modeling results of the effect of the acidic solution conductivity on the performance for the µDMFCs with anode catalyst deposited only on the channel walls at ambient temperature and pressure and 1 M methanol at a flow rate of 0.1 ml/min..... 119 Figure 4.20 Modeling results of the effect of the acidic solution conductivity on the Figure 4.21 Modeling results of the effect of the solid-phase ionic conductivity on the performance of µDMFCs with anode catalyst deposited both on the membrane and

channel walls at ambient temperature and pressure and 1 M methanol/0.1 M sulfuric acid at a flow rate of 0.1 ml/min......121 Figure 4.22 Modeling results of the effect of the solid-phase ionic conductivity on the Figure 4.23 Modeling results of the current density generated from the catalyzed wall with different conductivities of the solid-phase ionic conductor for the µDMFCs of Figure Figure 4.24 Modeling results of the effect of the solid-phase ionic conductivity on performance for µDMFCs with anode catalyst deposited only on the channel walls at ambient temperature and pressure and 1 M methanol/0.1 M sulfuric acid at a flow rate Figure 4.25 Modeling results of the effect of the solid-phase ionic conductivity on the Figure 4.26 Modeling results of the effect of the channel dimensions on the performance of µDMFCs with anode catalyst deposited both on the membrane and channel walls Figure 4.27 Modeling results of the effect of the channel dimensions on the individual Figure 4.28 The modeled effect of the channel dimensions on the average methanol concentration at the anode catalyst layer on the membrane for the µDMFCs of Figure

Figure 4.29 The modeled effect of the channel dimensions on the average methanol
crossover flux at the interface of the membrane and cathode for the μ DMFCs of Figure
4.26
Figure 4.30 Modeling results of the effect of the channel dimensions on the performance
of μ DMFCs with anode catalyst deposited only on the channel walls under 1 M
methanol/0.1 M sulfuric acid solution at a flow rate of 0.1 ml/min 129
Figure 4.31 Modeling results of the effect of the channel dimensions on the individual
electrode performance for the µDMFCs of Figure 4.30
Figure 4.32 The modeled effect of channel dimensions on the ohmic potential losses in
the acidic solution for the µDMFCs of Figure 4.30

List of Symbols

Symbol	Description	Unit
A	Geometric electrode area	cm ²
а	Active specific surface area	1/m
а	Tafel constant	V
aj	Activity of species j	
b	Tafel slope	V/dec
C _m	Methanol concentration	mol/m ³
Co	Oxygen concentration	mol/m ³
C _{m, ref}	Reference methanol concentration	mol/m ³
Co, ref	Reference oxygen concentration	mol/m ³
D	Diffusion coefficient	m²/s
D _{m, a}	Diffusion coefficient of methanol in anode catalyst layer	m²/s
D _{m,m}	Diffusion coefficient of methanol in membrane	m²/s
D _{m,w}	Diffusion coefficient of methanol in water	m²/s
Do	Diffusion coefficient of oxygen in air	m²/s
E _{cell}	Cell potential	V
E_e	Equilibrium cell potential	V
E _{e,a}	Equilibrium anode potential	V
E _{e,c}	Equilibrium cathode potential	V
E°	Equilibrium potential at standard conditions	V
F	Faraday's constant	C/mol
G	Gibbs free energy	J/mol
ΔG	Change in Gibbs free energy	J/mol
ΔG^o	Change in Gibbs free energy at standard conditions	J/mol
ΔH	Change in enthalpy	J/mol
h	Channel height	mm
1	Current	А
i	Current density	A/m ²
j	Volumetric current density	A/m ³

K	Permeability of cathode GDL	m²
k m, j	Mass transfer coefficient of species j	m/s
1	Channel length	mm
Μ	Molecular mass	kg/mol
т	Mass	kg
N _m	Methanol flux	mol/(m ² s)
n	Number of electrons transferred	
n _{RDS}	Number of electrons transferred in the rate determining step	
Δn_g	Change in number of mole of gaseous species	
n _d	Electro-osmotic drag coefficient	
Ρ	Pressure	Pa
R	Gas constant	J /(mol K)
Relectron	Electrical resistance	Ω
Rion	Ionic resistance	Ω
R_t	Ohmic resistance	Ω
S	Source term	
ΔS	Change in entropy	J /(mol K)
Sj	Stoichiometric coefficient of species j	
Т	Temperature	К
Q	Flow rate	m³/s
и	Velocity	m/s
ΔV_g	Change in volume of gaseous species	m ³
W	Electric work	J/mol
W	Weight percent	
W	Channel width	mm
X	Mole fraction	
Zj	Valence of ion j	
α	Charge transfer coefficient	
β	Reaction order	
β	Symmetry factor	
γ	Correction factor for parasitic current	

3	Porosity of porous media					
E _{CL}	Porosity of catalyst layer					
€ _{CL,} ion	Volume fraction of ionomer within catalyst layer					
E GDL	Porosity of GDL					
E _{mem}	Porosity of membrane					
ερ	Volume fraction of the inert phase					
η_{actual}	Actual operating efficiency					
η_{Co}	Columbic efficiency					
η_d	Mass transfer overpotential	V				
η_{fuel}	Fuel utilization coefficient					
η _{ohm}	Ohmic overpotential	V				
ηs	Surface overpotential	V				
η _{s,a}	Anodic activation overpotential	V				
$\eta_{s,c}$	Cathodic activation overpotential	V				
$\eta_{\textit{thermo}}$	Thermodynamic efficiency					
η_V	Voltage efficiency					
λ_{j}	Ionic molar conductivity of ion j	S m²/mol				
λ_w	Water content in Nafion membrane					
μ	Dynamic viscosity	Pa⋅s				
ρ	Density	kg/m ³				
σ	Conductivity	S/m				
Т	Sample thickness	mm				
$oldsymbol{arphi}_l$	Local electrolyte potential	V				
$oldsymbol{arphi}_{ extsf{s}}$	Local electrical potential	V				
ω	Mass fraction					

List of Abbreviations

3D	Three dimensional
AFC	Alkaline fuel cell
ССМ	Catalyst coated membrane
DLFC	Direct liquid fuel cell
DMFC	Direct methanol fuel cell
EIS	Electrochemical impedance spectroscopy
GDL	Gas diffusion layer
LFFC	Laminar flow fuel cell
MEA	Membrane electrode assembly
MCFC	Molten carbonate fuel cell
OCV	Open circuit voltage
PAFC	Phosphoric acid fuel cell
PEMFC	Polymer electrolyte membrane fuel cell
PEMFC	Proton exchange membrane fuel cell
RAFC	Redox anode fuel cell
SHE	Standard hydrogen electrode
SOFC	Solid oxide fuel cell

Acknowledgments

I would like to express my sincere appreciation towards the people who have supported me during my Ph.D. studies.

Firstly, I would like to express my sincere gratitude to my supervisors, Professors Fariborz Taghipour and David P. Wilkinson, for your valuable and professional guidance, and continuous encouragement, patience, and support.

My appreciation also goes to Professors John Madden and Vikramaditya G. Yadav for serving as my thesis committee members and your insightful suggestions.

I would like to thank Greg Afonso for fabricating the fuel cell components, Baizeng Fang, Kevin Reilly, Arman Bonakdapour, Saad Dara, Winton Li, and Blaise Pinaud for sharing your valuable experience.

I offer my gratitude to my colleagues in Labs 626, 618 and friends in CHBE, for your companion and encouragement.

I would like to acknowledge the China scholarship council (CSC) for the valuable financial support.

I would like to give special thanks to my parents and my family who always love and support me unconditionally.

Finally, I would like to thank the Great Creator. Because of your great mercy, surpassing grace and unconditional love, I believe I can do it with blessed hope no matter what challenges I faced during each step of this thesis.

Dedicated to my family

Chapter 1: Introduction

The global energy need has projected a growth of 30% by 2040 according to the World energy outlook 2016 by the International Energy Agency¹. Also, the emission of greenhouse gas and other pollutants from fossil fuel results in an increased worldwide concern. The increased energy demand and reduction of non-renewable resources inspire the search for substitutable resources and alternative approaches to increase the efficiency of energy conversion and sustainability.

Fuel cells are an attractive approach to improve the efficiency of energy conversion for the future energy demand as they can directly transform the chemical energy of a fuel into electrical power through an electro-chemical reaction². As a result of avoiding the intermediate energy conversion stages in a heat engine, fuel cells can potentially reach a higher efficiency than the conventional power generation system. Additionally, fuel cells emit zero or very small amount of air pollutants.

However, each type of fuel cell still has its weaknesses that must be addressed before widespread commercialization³. In order to make fuel cell competitive with the conventional power generation technologies, appropriate fuel cell designs for different potential applications are required to get sufficient power and reduce the cost.

1.1 A brief background of fuel cell technology

The first fuel cell was effectively demonstrated by Welsh scientist Sir William Robert Grove in 1839⁴. He conducted the fuel cell experiment in a gas voltaic battery in which

two platinum electrodes were placed in two separate tubes of hydrogen and oxygen, and the tubes were inverted in a container with a dilute sulfuric acid solution as the electrolyte (Figure 1.1).



Figure 1.1 Grove's gas voltaic battery.

This gas battery includes the three essential elements of a fuel cell an anode, a cathode, and an electrolyte, which can generate a current through the electrochemical reactions occurring at the electrodes. At the anode, hydrogen is oxidized, producing protons and electrons. The protons pass through the electrolyte toward the cathode. The electrons travel through an external circuit to the cathode, generating the electric current. At the cathode, protons and electrons and electrons and electrons the importance of the triple phase contact between the reactant, electrode, and electrolyte. Since the triple phase contact area in the Grove cell was very small, only a small area of the electrode at the gas-liquid interface was active, and also,

the large distance between the electrodes led to a high electrolyte resistance, only a very small electric current could flow through the external circuit.

The half-cell and overall reactions of the fuel cell are shown as follows:

Anode:
$$2H_2 \to 4H^+ + 4e^ E^o = 0 V vs. SHE$$
 (1.1)

Cathode:
$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$
 $E^o = 1.229 \text{ V vs. SHE}$ (1.2)

Overall: $2H_2 + O_2 = H_2O$. $E^o = 1.229 V$ (1.3)

The turning point for fuel cell technology was the first commercial application of the fuel cell in the 1960s when solid polymer fuel cells and alkaline fuel cells were used to generate electrical power for the National Aeronautic Space Administration (NASA) Gemini and Apollo Missions respectively⁵. Since those days, great effort was made on developing and studying the fuel cell, and the research on fuel cells has accumulated valuable knowledge for subsequent research. Since fuel cells can offer a highly efficient, simple and clean way of generating electrical energy, this technology is considered as an attractive alternative power generation system in three main applications, including portable devices, electric vehicles, and primary and backup power generations. A few different types of fuel cells have been developed in the twentieth century. Table 1.1 lists the different types of fuel cells classified primarily by the electrolyte, which dictates the operating temperature range, the fuel needed, and the catalyst needed in the oxidation reaction. All of these factors determine the most appropriate applications for each type of fuel cell.

Table 1.1 Comparison of fuel cell technologies^{5–7}.

Fuel cell types		Fuel	Common Electrolyte	Operating Temperature	Electrical Efficiency	Typical stack size
PEMFC	Proton exchange membrane fuel cell	H ₂	Solid polymer membrane	<120ºC	40~60%	<1- 100 kW
DMFC	Direct methanol fuel cell	CH₃OH	Solid polymer membrane	60~200⁰C	40%	0.001- 100 kW
AFC	Alkaline fuel cell	H ₂	Aqueous KOH in a matrix or alkaline polymer membrane	90~100ºC	60%	1-100 kW
PAFC	Phosphoric acid fuel cell	H ₂ , Natural gas, biogas	H₃PO₄ in a matrix or polymer membrane	150~200⁰C	40%	5-400 kW
MCFC	Molten carbonate fuel cell	H ₂ , Natural gas, biogas, coal gas	Li ₂ CO ₃ or K ₂ CO ₃ in a matrix	600~700ºC	50%	300 kW- 3 MW
SOFC	Solid Oxide fuel cell	H ₂ , Natural gas, biogas, coal gas	Yttria stabilized zirconia (YSZ)	500~1000⁰C	60%	1 kW- 2 MW

Among all the fuel cells, the low-temperature fuel cells like the polymer electrolyte membrane fuel cell (PEMFC) are most suitable for transportation applications to power different kinds of vehicles, such as automobiles, buses, forklifts, motorcycles, ships, and so on. The direct methanol fuel cell (DMFC) was first developed jointly by the NASA Jet Propulsion Laboratory and the University of Southern California in 1990³. It is an attractive choice for portable device applications, such as cell phones and laptops. The

high-temperature fuel cells, including phosphoric acid, molten carbonate and solid oxide fuel cells are suitable for large-scale stationary applications. These fuel cells can be used as primary and backup electrical power for medical, educational, and residential buildings, and also as the primary electricity in an isolated area inaccessible to the electrical grid.

1.2 Basic principles of fuel cell design

For the design of fuel cells, there are some basic governing laws, such as mass, momentum and charge conservation, and thermodynamics. The distributions of potential, current and species in the fuel cell are all limited by these laws.

1.2.1 Thermodynamics of the fuel cell

1.2.1.1 Standard cell and electrode potentials

The standard fuel cell potential is the maximum cell voltage under standard conditions of 298 K, 1 atm, and the activities of all the reactants and products are equal to 1. For any half-cell electrode reactions, the general stoichiometry equations can be written as:

$$ne^- \Leftrightarrow \sum_j s_j M_j$$
 (1.4)

where *n* is the number of electrons transferred in the half-cell reaction; M_j is the chemical species j; s_j is the stoichiometric coefficient of the species j. For reduced species, s_j is positive, while for oxidized species, s_j is negative. By convention, reduction reactions occur at the cathode and oxidation reactions occur at the anode.

Through the electrochemical reaction in the fuel cell, chemical energy stored in a fuel can be converted to electrical energy. The energy change of the chemical species through the electrode reaction could be defined by calculating the difference of the change in Gibbs free energy of formation. The changes in Gibbs free energy of formation in the anode or cathode reactions can be written as:

$$\Delta G_{a \text{ or } c} = \sum_{j} s_{j} \cdot G_{j} \tag{1.5}$$

where G_i is the Gibbs free energy of formation of species j.

The chemical energy is released to produce electric work. The change in Gibbs free energy of formation of the reaction is equal to the thermodynamic maximum electric work that the reaction could produce.

$$W_{max} = -\Delta G_{a \ or \ c} \tag{1.6}$$

The standard electrode potentials E_a^o and E_c^o can be calculated through the change in Gibbs free energy of formation of the half-cell reactions.

$$E_a^o = \frac{-\Delta G_a^o}{nF} \tag{1.7}$$

$$E_c^o = \frac{-\Delta G_c^o}{nF} \tag{1.8}$$

where *n* is the number of electrons transferred per molecule of reactant; *F* is Faraday's constant, equal to the charge of one mole of electrons (96485 C/mol). The negative sign is due to the convention that a power source should have a positive cell potential and a negative Gibbs free energy of formation.

The standard cell potential E° can be calculated through the change in Gibbs free energy of the overall reaction.

$$E^{o} = \frac{-\Delta G^{o}}{nF} \tag{1.9}$$

where ΔG^{o} is the change of Gibbs free energy of the entire reaction at standard conditions.

$$\Delta G^o = G^o_{products} - G^o_{reactants} \tag{1.10}$$

The standard cell potential can also be expressed as the difference of the half-cell standard potentials.

$$E^{o} = E_{c}^{o} - E_{a}^{o} \tag{1.11}$$

1.2.1.2 The effect of concentration

Under the non-standard reference condition, the ideal maximum cell voltage is called the equilibrium cell potential E_{e} .

$$E_e = \frac{-\Delta G}{nF} \tag{1.12}$$

When the activity is not 1 for all the species, the change of the Gibbs free energy of the reaction can be expressed as:

$$\Delta G = \Delta G^{o} + RT ln \prod_{j} a_{j} s_{j}$$
(1.13)

where ΔG^o is the standard Gibbs free energy of the reaction; *R* is the gas constant; T is temperature; s_j is the stoichiometric coefficient of the species j; a_j is the activity of the species j.

Using equations 1.9 and 1.12 to substitute ΔG° and ΔG in equation 1.13 results in the Nernst equation.

$$E_e = E^o - \frac{RT}{nF} \ln \prod_j a_j s_j \tag{1.14}$$

where E_e is the equilibrium electrode potential, and E^o is the standard electrode potential.

1.2.1.3 The effect of temperature

The temperature change can also cause a Gibbs free energy change, resulting in a change in the equilibrium electrode potential. In thermodynamics, the Maxwell equation can describe the change in Gibbs free energy with temperature.

$$\frac{\partial \Delta G}{\partial T} = -\Delta S \tag{1.15}$$

where ΔS is the entropy change of the reaction.

The relationship of the equilibrium electrode potential and temperature can be written as:

$$\frac{\partial E_{e,T}}{\partial T} = \frac{\Delta S^o}{nF} \tag{1.16}$$

When assuming ΔS remains the same in a small temperature range, equation 1.16 can be easily integrated between 298 K and the actual temperature.

$$E_{e,T} = E^0 + \frac{\Delta S}{nF} (T - 298)$$
(1.17)
1.2.1.4 The effect of pressure

Under non-standard pressure, the Maxwell equation can describe the change in Gibbs free energy with pressure.

$$\frac{\partial \Delta G}{\partial P} = \Delta V_g \tag{1.18}$$

where ΔV_g is the volume change of gas species in the reaction.

The relationship of the equilibrium electrode potential and pressure can be written as:

$$\frac{\partial E_{e,P}}{\partial P} = -\frac{\Delta V_g}{nF} \tag{1.19}$$

When assuming an ideal gas, ΔV_g can be expressed as:

$$\Delta V_g = \frac{\Delta n_g RT}{P} \tag{1.20}$$

Then equation 1.19 can be integrated between 1 atm and the actual pressure to give:

$$E_{e,P} = E^o - \frac{\Delta n_g RT}{nF} \ln\left(\frac{P}{1 a t m}\right)$$
(1.21)

1.2.1.5 Thermodynamic efficiency

The thermodynamic efficiency of the fuel cell η_{thermo} is defined as⁸:

$$\eta_{thermo} = -\frac{\Delta G}{\Delta H} = -\frac{nFE_e}{\Delta H} \tag{1.22}$$

where ΔH is the change of enthalpy, and n is the number of electrons transferred per molecule of reactant.

1.2.2 Fuel cell irreversibilities

The equilibrium potential is the ideal maximum cell voltage when the electrochemical reaction is ideally reversible. When operating a fuel cell practically, the actual cell potential is always less than E_e even at the open circuit condition due to various irreversibilities. The irreversibility is also referred to as overpotential or losses. A polarization curve shown in Figure 1.2 is the most common method to characterize the performance of a fuel cell by displaying a plot of the cell voltage versus current density. The three regions shown in the figure are divided according to the dominant causes of voltage drop in each region. For the low current density region, activation losses usually contribute most of the voltage drop, while for the high current region, mass transport losses are most important. For the intermediate region, the ohmic losses are dominant.



Figure 1.2 Polarization curve for a fuel cell operated at low-temperature.

The relation of the cell voltage and equilibrium potential can be expressed as:

$$E_{cell} = E_e - \eta_{s,a} + \eta_{s,c} - \eta_{d,a} + \eta_{d,c} - \eta_{ohm}$$
(1.23)

where $\eta_{s,a}$ and $\eta_{s,c}$ are the surface overpotentials (activation losses) of anode and cathode, respectively; $\eta_{d,a}$ and $\eta_{d,c}$ are the mass transfer overpotentials of anode and cathode, respectively; η_{ohm} is the ohmic overpotential.

1.2.3 Activation losses

The activation overpotential is due to the slow reaction occurring on the electrode. So part of the voltage is lost to lower the activation energy of the reaction to accelerate the electrochemical reaction.

The Bulter-Volmer equation is often used to describe the activation losses of the electrode reaction under pure kinetic control.

$$i = i_0 \left[exp\left(\frac{\alpha_a F}{RT} \eta_s\right) - exp\left(-\frac{\alpha_c F}{RT} \eta_s\right) \right]$$
(1.24)

where *i* is current density; i_0 is the exchange current density; η_s is the surface overpotential, $\eta_s = E - E_e$; and α_a and α_c are the transfer coefficients for the anode and cathode.

$$\alpha_a = (1 - \beta) n_{RDS} \tag{1.25}$$

$$\alpha_c = \beta n_{RDS} \tag{1.26}$$

where β is the symmetry factor, and n_{RDS} is the number of electrons transferred in the rate determining step.

When $|\eta_s|$ > 0.025 V, the Bulter-Volmer equation can be simplified as:

$$i = i_a = i_0 \left[exp\left(\frac{\alpha_a F}{RT} \eta_s\right) \right]$$
(1.27)

$$i = i_c = i_0 \left[-exp \left(-\frac{\alpha_c F}{RT} \eta_s \right) \right]$$
(1.28)

where i_a is the anodic current, and i_c is the cathodic current.

The Tafel equation can be written as:

$$|\eta_s| = b \log|i| + a \tag{1.29}$$

$$b = \frac{2.303RT}{\alpha F} \tag{1.30}$$

$$a = -\frac{2.303RT}{\alpha F} logi_0 \tag{1.31}$$

The exchange current density i_0 and the Tafel slope b are vital parameters in controlling the reaction rate of the fuel cell. It is desired to make the electrode catalyst with a high i_0 and a low Tafel slope.

1.2.4 Ohmic losses

The Ohmic losses (η_{ohm}) depend on the resistances to the electron flow through all the electrically conductive components and ion flow through the electrolyte. Thus, the overall fuel cell resistance (R_t) includes both electric and ionic resistances as shown in equation 1.32. In fuel cells, the ohmic overpotential is mainly caused by the resistance of the electrolyte.

$$\eta_{ohm} = i \cdot R_t = i(R_{electron} + R_{ion}) \tag{1.32}$$

1.2.4.1 Liquid electrolyte

The ionic conductivity of the liquid electrolyte depends on the concentration, temperature and the fraction of inert phase

When the concentration of the electrolyte is less than 1 mol/m³, the conductivity can be given as:

$$\sigma = \sum_{j} \lambda_j C_j \tag{1.33}$$

$$\lambda_j = \frac{z_j^2 F^2}{RT} D_j \tag{1.34}$$

where σ is the conductivity of the electrolyte; λ_j is the ionic molar conductivity of ion j; C_j is the concentration of ion j; z_j is the valence of ion j; D_j is the diffusion coefficient of ion j.

When the concentration of the electrolyte is high (typically between 1 M to 10 M), the Casteel-Amis equation⁹ shown below can be used to describe how the ionic conductivity change with the concentration and temperature.

$$\sigma = \sigma'_{max} \left(\frac{w}{w'_{max}}\right)^x exp\left[y(w - w'_{max})^2 - \frac{x}{w'_{max}}(w - w'_{max})\right]\sigma'_{max}\sum_j \lambda_j C_j$$
(1.35)

$$\sigma'_{max} = \sigma_{max1} + \sigma_{max2}T \tag{1.36}$$

$$w'_{max} = w_{max1} + w_{max2}T (1.37)$$

where σ is the conductivity of the electrolyte; w is the weight percent; w_{max1} and w_{max2} are weight percent constants of the electrolyte; σ_{max1} and σ_{max2} are conductivity constants of the electrolyte; x and y are constants of the electrolyte.

When inert phases like gas bubbles or solid particles appear in the electrolyte, the relationship of the conductivity and volume fraction of the inert phase can be estimated by Maxwell (1.38) and Meredith-Tobias (1.39) equations^{10, 11}.

$$\frac{\sigma}{\sigma_0} = \frac{1 - \varepsilon_p}{1 + \varepsilon_p/2} \qquad \qquad \varepsilon_p \le 0.6 \tag{1.38}$$

$$\frac{\sigma}{\sigma_0} = 8 \frac{(1 - \varepsilon_p)(2 - \varepsilon_p)}{(4 + \varepsilon_p)(4 - \varepsilon_p)} \qquad \qquad \varepsilon_p > 0.6 \qquad (1.39)$$

where σ is the effective conductivity; σ_0 is the conductivity without an inert phase; ε_p is the volume fraction of the inert phase.

In a porous medium with a porosity of ε , assuming all the pores are filled with a liquid electrolyte, the effective conductivity of the electrolyte can be calculated by the Bruggeman equation¹².

$$\sigma = \sigma_0 \varepsilon^{1.5} \tag{1.40}$$

1.2.4.2 Solid electrolyte: Ion exchange membrane

Nafion® developed by DuPont in the late 1960s is the predominant commercially available proton exchange membrane because of its excellent chemical, thermal and mechanical stability¹³. Nafion is based on perfluorosulfonic acid (PFSA) ionomers consisting of hydrophobic tetrafluoroethylene (Teflon) backbone groups modified with hydrophilic sulfonate groups. Protons on the sulfonic acid group can hop between the fixed charged sites.

The ionic conductivity of the Nafion membrane is determined by water content and temperature¹⁰.

$$\sigma = (0.46\lambda_w - 0.25)exp\left[-1190\left(\frac{1}{T} - \frac{1}{298}\right)\right]$$
(1.41)

where σ is the ionic conductivity of Nafion; λ_w is the water content; T is the operating temperature.

1.2.5 Mass Transport losses

Since the fuel is being consumed at the surface of the electrode, the concentrations of the fuel and the product on the surface and in the bulk are different. The mass transport losses result from insufficient fuel and oxidant on the surface of the electrode. The region near the electrode surface where there is a concentration gradient between the surface concentration and bulk concentration is referred as the diffusion boundary layer since the electro-active species are mainly transported by diffusion. The mass transport overpotential can be defined as:

$$\eta_d = \frac{RT}{nF} \sum_j \ln\left(1 - \frac{i}{i_{L,j}}\right) \tag{1.42}$$

where η_d is the mass transfer overpotential, and $i_{l,j}$ is the limiting current density of species j.

When the diffusion resistance is dominant, the limiting current density is approximated as follow¹⁰.

$$i_{L,j} = -\frac{nF}{s_j} \frac{D_j}{\tau_D} C_j = \frac{nF}{s_j} k_{m,j} C_j$$
(1.43)

where τ_D is the thickness of the diffusion boundary layer; D_j is the diffusion coefficient of species j; $k_{m,j}$ is the mass transfer coefficient; C_j is the bulk concentration.

1.2.6 Fuel crossover losses

When a fuel cell is put to use, some fuel will cross the electrolyte membrane from the anode to cathode. The fuel can directly react with oxygen on the catalyst, generating a mixed potential on the cathode, which can significantly drop the open circuit potential of the fuel cell.

1.2.7 Efficiency of the fuel cell

When a fuel cell is put to use, the actual cell potential is less than the equilibrium potential. The difference can be evaluated by the voltage efficiency, the ratio between the actual cell potential and the equilibrium potential¹⁴.

$$\eta_V = \frac{E_{cell}(i)}{E_e} \tag{1.44}$$

The actual number of electrons transferred cannot always reach the theoretical number according to the stoichiometry, especially in the reaction involving multi-electrons per molecule of fuel, such as methanol (n=6) and ethanol (n=12). The columbic efficiency is defined as the ratio of the number of electrons.

$$\eta_{Co} = \frac{n_{actual}}{n} \tag{1.45}$$

To get the actual operating efficiency, the actual cell potential at a certain current density (usually at the current density with the maximum power density) and the actual number of electrons transferred are substituted into equation 1.22.

$$\eta_{actual} = -\frac{n_{actual} F E_{cell}(i)}{\Delta H} = \eta_{thermo} \cdot \eta_V \cdot \eta_{Co}$$
(1.46)

The fuel utilization coefficient is defined as the ratio of the mass of reacted fuel to the mass of input fuel.

$$\eta_{fuel} = \frac{m_{reacted}}{m_{input}} \tag{1.47}$$

1.3 The direct methanol fuel cell

The lithium-ion (Li-ion) rechargeable battery powers most of the current portable devices. The volumetric energy density of Li-ion batteries is 400 Wh/L, and the theoretical specific energy density is 410 Wh/kg¹⁵. The capacity limitation makes Li-ion batteries challenging to meet the increasing demands for future power sources with a higher energy density and longer lasting time. Hydrogen-fed proton exchange fuel cells can achieve high efficiency at relatively low temperature, however, miniaturizing the

hydrogen-fed PEMFC is still quite a challenging task as safe and reliable storage and delivery of hydrogen in a small size is a relatively unsolved problem¹⁶.

Liquid hydrocarbon fuels with high energy densities like methanol that can be used in fuel cells are expected to improve the energy density of the power source. Fuel cells can generate electricity through electrochemical reactions to convert chemical energy stored in the fuel into electrical energy. Therefore, they potentially can be operated with much longer cell lifetime than batteries¹⁷. Among all the direct hydrocarbon fuel cells, the direct methanol fuel cell (DMFC) is considered to be one of the most promising and attractive to power portable devices^{8,17–19} due to its better kinetics than the other hydrocarbon fuels.

Methanol is a low-cost liquid fuel and has a high energy density of 4384 Wh/L²⁰. μ DMFCs also have several other characteristics which are beneficial to portable applications, such as being lightweight, operation at low temperatures, and easy fuel storage and transportation²¹. Furthermore, μ DMFCs do not require hours to recharge; instead, instantaneous recharging can occur by replacement of a fuel cartridge. As a result, many μ DMFCs prototypes are developed by different companies as an alternative power source for portable electronic devices (Table 1.2).

Company	Maximum power density and total	Potential application
	power	
Samsung SDI ²²	12-20 W, 120 Wh	Laptop
Toshiba ²³	30 mW/cm², 5 W at 30~40°C	Mobile phone
NEC ^{20, 23}	70 mW/cm², 14 W	Laptop
Antig ²³	12 W	Portable devices
SFC Smart Fuel	25 W at sub-zero to 40° C	Laptop and portable
Cell GmbH ²³		devices
MTI Micro-Fuel	800 mW, 35 Wh	Mobile phone
cells ²⁴		
Motorola Labs ²⁴	100 mW	Mobile phone

Table 1.2 Micro-Direct methanol fuel cells developed by different companies.

Figure 1.3 shows the fundamental operating principles of the direct methanol fuel cell. At the anode side, an aqueous methanol solution is supplied. 1 mole of methanol in the presence of 1 mole of water is oxidized in the anode catalyst layer, producing 1 mole of carbon dioxide, 6 moles of protons and 6 moles of electrons. The protons and electrons pass through the polymer electrolyte membrane and external power circuit to the cathode, respectively. At the cathode, 1.5 moles of oxygen are reduced by 6 moles of protons and 6 moles of water.



Figure 1.3 Operation principles of the direct methanol fuel cell.

The electrochemical equations for the half-cell and overall reactions in DMFCs are shown below:

Anode:
$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^ E^o = 0.016 \text{ V vs. SHE}$$
 (1.48)

Cathode:
$$\frac{3}{2}O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$$
 $E^o = 1.229 \text{ V vs. SHE}$ (1.49)

Overall:
$$CH_3OH + \frac{3}{2}O_2 \to CO_2 + 2H_2O$$
 $E^o = 1.213 \text{ V.}$ (1.50)

However, the poor performance of μ DMFCs compared to hydrogen-fed PEMFCs has severely hindered the commercialization of μ DMFCs. Several major limitations remain to be solved before the future commercialization of μ DMFCs, such as high methanol crossover and slow kinetics of the methanol electro-oxidation reaction. In order to improve the performance, a goal for the micro fuel cell design is to increase the active surface area of the electrode to provide more effective triple phase regions where the electrochemical reactions of the proton/electron/methanol can occur^{25,26}. Increasing the catalyst loading may yield a larger active surface area, but the active surface area does not always improve with the catalyst loading. After reaching a certain catalyst loading, the performance begins to decline with a further increase in the loading²⁷. This is because increasing the catalyst loading is often associated with a thicker electrode, producing a steeper concentration gradient for methanol and causing a detrimentally higher diffusion/penetration resistance for methanol reactant supply and carbon dioxide removal¹⁶.

1.3.1 Micro DMFC architectures

The micro fuel cells are miniaturized fuel cells which can be applied as power sources for portable low-power electronic devices, such as mobile phones and laptops with a maximum power ranging from 1 W to 50 W²⁴. The size of micro fuel cells ranges from several square millimeters to 1000 square millimeters². Small size fuel cells are not just merely scaled-down large size fuel cells. The micro fuel cells must have adequate power while simultaneously meeting the criteria for portable device applications, such as a very small size and being very lightweight.

The basic components in micro fuel cells include current collectors, flow field plates, diffusion layers, catalyst layers and a proton exchange membrane. Currently, two basic design configurations are employed in micro fuel cells²⁸, i) the traditional bipolar design, and ii) the planar design. Both designs are depicted in Figure 1.4. In the bipolar design, the membrane electrode assembly (MEA) is sandwiched between two flow field plates to separate the fuel and oxidant supply. The MEA is the core part, which includes a proton exchange membrane (PEM), anode and cathode catalyst layers and diffusion layers. This design demands all the parts to be built individually and then put together.

Unlike the arrangement in a bipolar design, the anode and the cathode are on the same side of the PEM in a planar design. This design is more appropriate for a monolithic integration and requires a large surface area to show a comparative performance to the bipolar design.



Figure 1.4 Two basic designs of μ DMFCs (a) bipolar, (b) planar²⁹.



Figure 1.5 Schematic of a silicon-based planar micro direct methanol fuel cell: (a) top-view (b) cross-sectional view of the design³⁰. Reprinted from Electrochemistry Communications, 6(6), Shinji Motokawa, Mohamed Mohamedi, Toshiyuki Momma, Shuichi Shoji, Tetsuya Osaka, MEMS-based design and fabrication of a new concept micro direct methanol fuel cell (μ -DMFC), 562-565, Copyright (2004), with permission from Elsevier.

In a few planar fuel cells, catalyst was directly supported on the walls of the channels. Motokawa³⁰ first proposed the planar design with catalyst supported on the channel walls and tested the concept in a μ DMFC. Two parallel anodic and cathodic microchannels were fabricated on a planar silicon wafer as shown in Figure 1.5. The depth of the channel, the width of the channel, and the distance between the two channels were all equal to 100 μ m. A 100 nm gold layer was evaporated on the walls of the microchannels as a current collector. Catalyst layers were deposited on the gold by electroplating. The maximum power density was 0.78 mW/cm² by using a fuel solution (2 M CH₃OH/0.5 M H₂SO₄) and an oxidant solution (O₂-saturated/0.5 M H₂SO₄) at room temperature. D'Urso³¹ developed a planar µDMFC on a polymeric substrate with anodic and cathodic channels covered by Nafion membrane. Gold layers were sputtered in the channel to guarantee the electrical conductivity. A thin space with a distance of 0.25 mm and 0.5 mm between the anode and cathode channels were not covered by gold. To promote the reactions, Pt-Ru and Pt catalysts were deposited onto the walls of the fuel channels and air channels, respectively. The best performance achieved a maximum power density of 1.3 mW/cm² when the catalyst was only coated on a dry membrane with a distance between the anode and cathode of 0.25 mm. The performance declined significantly when the catalyst was deposited only on the walls of the channels or on both the dry membrane and channel's walls with a larger distance (0.5 mm) between the anode and cathode. The electrochemical impedance spectroscopy (EIS) spectrum demonstrated that the performance is limited by a large mass transfer resistance and a charge transfer resistance.

Shen³² constructed a planar µDMFC consisting of parallel anodic and cathode microchannels in a glass plate. The catalyst was sprayed onto a 100 nm gold layer, which was evaporated onto the micro-channels' walls, proceeded by a 0.5 nm chromium layer just beneath the gold to promote adhesion. The maximum power density was 0.5 mW/cm² by supplying a 1 M CH₃OH/0.5 M H₂SO₄ solution as the fuel and a 0.01 M H₂O₂/0.5 M H₂SO₄ solution as the oxidant.

The low-temperature microfluidic fuel cell was invented in 2002. In this membranes-less fuel cell, all the reactions, reactant delivery, and product removal happen in a single

micro-channel without the physical barrier of a membrane to separate cathode and anode flow fields^{33–37}. The electrodes are usually integrated on the walls of a channel. The design is also called a laminar flow fuel cell (LFFC)³⁴ since the design takes advantage of laminar flow in a micro-channel to separate the fuel and oxidant. As shown in Figure 1.6, two parallel co-laminar streams of fuel and oxidant flow in a channel by adjusting geometry and flow operating conditions. This approach aims to eliminate the requirement for a proton exchange membrane, removing membrane issues such as the change in size with water content.



Figure 1.6 Schematic of a design of laminar flow fuel cell³⁴. Reprinted from Journal of Power Sources, 128(1), Eric R. Choban, Larry J. Markoski, Andrzej Wieckowski, Paul J.A. Kenis, Microfluidic fuel cell based on laminar flow, 54-60, Copyright (2004), with permission from Elsevier.

This approach has been studied by several researchers. R. Ferrigno³⁸ first introduced a proof of concept for a vanadium-based fuel cell based on LFFC. A maximum power density of 38 mW/cm² was achieved. Nevertheless, the fuel utilization was less than 10% due to the slow diffusion rate of reactants to the catalyst reaction sites. E.R Choban³⁹ developed a similar Y-shaped laminar flow fuel cell. The cell was operated with an anode stream of 1 M methanol mixed with 0.5 M H₂SO₄ and a cathode stream

of 0.5 M H₂SO₄ solution saturated with oxygen. The maximum power density was 2.8 mW/cm² when the anode catalyst loading is 2 mg/cm² unsupported Pt/Ru nanoparticles and the cathode catalyst loading is 2 mg/cm² unsupported Pt nanoparticles. This cell was limited by mass transport of oxygen as both the oxygen concentration (2-4 mM) and diffusion coefficient $(2 \times 10^{-5} \text{ cm}^2/\text{s})$ in aqueous media is much lower than in air. Jayashree⁴⁰ improved the design by using an air-breathing cathode to eliminate the mass transfer limitation of dissolved oxygen in solutions. When the anode stream was 1 M methanol/0.5 M H₂SO₄ and the electrolyte stream on the cathode side was 0.5 M H_2SO_4 , a maximum power density of 11.8 mW/cm² was produced at room temperature. The flow rate and cell geometry were strictly restricted to form steady laminar flow. D.Whipple⁴¹ implemented a methanol tolerant catalyst Ru_xSe_y in a laminar flow fuel cell. The performance of fuel cells with or without methanol in the cathode streams was tested. When methanol (1 M-15 M) was presented in the cathode stream, the peak power densities of fuel cells with the Pt cathodes showed a 67-88% decrease, while Ru_xSe_v did not show any drop. The electrolyte stream could be removed when using selective cathode catalyst. The main problems for LFFC are the limitation of fuel mass transfer in the depletion boundary layer and mixing of two streams in the channel, resulting in low fuel utilization. Additionally, the difference between the densities of the two streams limits the operation of the fuel cell to only a specific orientation, making it impractical for integration into mobile devices. It is evident that although there have been several attempts in the development of miniaturized fuel cells with parallel flows, major issues such as the inter-diffusion of fluid streams and the mass transfer limit their application.

1.3.2 Catalyst loading process

1.3.2.1 Catalyst loading methods

The catalyst loading process has a significant influence on the efficiency of the μ DMFC⁴². Many methods have been developed, including spraying, sputtering, painting, spreading, decaling, screen-printing, electro-deposition, evaporative deposition, and chemical plating. The commonly used process is spraying (also called wet spraying), a process that uses a spray gun to load the catalyst⁴³⁻⁴⁵. Sputtering is a momentum transfer process used to form a thin catalyst film⁴⁶. This method is more accurate than all the other loading process and offers the best catalyst utilization. The loading is usually lower than 1 mg/cm² with a thickness in the range of 5 nm to 1000 nm. Pt-Ru can be sputtered directly onto both the membrane and carbon paper^{47,48}. The electro-deposition method has also been adopted for the μ DMFC in a few cases⁴⁹⁻⁵¹.

1.3.2.2 Anode catalyst loading amount

Shimizu²⁷ investigated various loadings of Pt ranging from 0.5 to 5 mg/cm² for the carbon supported Pt-Ru (30.1 wt.% Pt, 23.3 wt.% Ru) anode for passive DMFCs. The current density increased when the Pt loading was increased from 0.5 to 2.5 mg/cm² as expected. The performance began to decline with a further increase in the loading. This drop is because increasing the catalyst loading produces a thicker electrode, resulting in a steeper concentration gradient for the methanol. Bae⁵² presented the performance of passive DMFCs under various Pt-Ru catalyst loadings from 4 to 10 mg/cm². When the anode catalyst loadings were equal or higher than 6 mg/cm², the maximum power density was almost the same. Havranek⁵³ observed that the current density was

dramatically increased when the Pt-Ru loading was increased from a lower value to a critical value for half-cell measurements. The critical value was determined to be about 3 mg/cm² at 40°C, 2 mg/cm² at 60°C, and 1.5 mg/cm² at 80°C. After exceeding the critical value of the catalyst loading, the anode performance was only slightly enhanced. These studies have shown that there exists an optimum loading versus the performance as a result of the interplay between the number of active sites and methanol supply.

1.3.3 Operating conditions of µDMFCs

1.3.3.1 Methanol concentration effect

Based on the stoichiometry of the methanol-oxidation reaction, the methanol concentration is 16.7 M when the molar ratio of methanol to water is 1:1. Even though the high methanol concentration can enhance the reaction kinetics and improve the energy density of fuel cells, it also increases the rate of methanol crossover to the cathode. To reduce the deleterious effects of methanol crossover, only dilute methanol solutions (i.e., 1 M) are usually used in DMFCs⁵⁴.

The effect of the methanol concentration in µDMFCs has been studied by several researchers. Zhang et al.⁵⁵ compared the performance of a fuel cell with a 0.48 cm² active area at methanol concentrations of 0.1 M, 0.5 M, 2 M, and 4 M. The best performance was found for a methanol concentration of 2 M. Zhang et al.⁵⁶ studied the performance of a fuel cell with a 0.64 cm² active area at methanol concentrations of 0.5 M, 1.0 M, 1.5 M, 2.0 M, and 2.5 M. The maximum current density improved with an increase of methanol concentration from 0.5 M to1.5 M, but drops with a further

increase of 1.5 M to 2.5 M. It was noted that the optimal methanol concentration (1.5 M) in the developed micro-sized DMFC is higher than the commonly used concentration (1 M) for large size DMFCs^{57,58}. A higher methanol concentration is desired for a micro DMFC than in a larger size DMFC due to the more difficult mass transfer of methanol in the micro-channel.

1.3.3.2 Air-breathing cathode

Since most of the portable electronic devices are for low-power applications, direct methanol fuel cells have been demonstrated with an air-breathing cathode^{59–61}. This passive mode can reduce the weight and size of a fuel cell by eliminating the need for auxiliary devices to supply the oxidant, such as gas compressors or fans. Oxygen from ambient air with a concentration of about 10 mM diffuses to the cathode catalyst layer with a diffusion coefficient of 2×10^{-5} m²/s as reported by Jayashree et al.³⁶. Litster et al.⁶² have shown that air-breathing cathodes can maintain a high oxygen mass fraction along the surface of the cathode, providing enough oxygen for the cathode reaction. This simplification with a passive air-breathing cathode makes the practical use of micro fuel cells as a commercial product possible.

However, generally, only mono-plane configurations are used as a passive air-breathing cathode due to the demand for an open cathode surface⁶². Separate fuel cells can be connected in series to achieve higher voltages⁶³.

1.4 The redox flow battery

The redox flow battery (RFB)^{64,65} is a relatively new rechargeable device for energy storage where rechargeability is provided by the redox species separated by a membrane within the cell. Unlike the conventional secondary battery where energy is stored in the electrode structure, redox flow batteries store energy in the flowing electrolytes containing active redox species⁶⁶. The total energy capacity of the RFB is dependent on the concentration and volume of the redox species.



Figure 1.7 Schematic and operating principles of a redox flow battery.

The basic operating principles of a redox flow battery are shown in Figure 1.7. The anolyte and catholyte stored in external storage tanks are recirculated through the anode and cathode flow fields separated by an ion exchange membrane, which is employed to transfer ions, prevent the electron flow, and separate the reductant and oxidant supplies. The architecture of RFBs is almost identical to the bipolar design of fuel cells where a membrane electrode assembly is sandwiched between two flow field

plates⁶⁷. The oxidation reaction on the anode and the reduction reaction on the cathode are very simple reversible reactions usually involving only one electron transfer. The fast reaction rates/kinetics allow RFBs to be operated under low-temperature conditions. Redox species reactions have fast electrochemical kinetics on non-platinum group metal (PGM) based catalysts, such as carbon and graphitic materials^{68–70}. Graphite, carbon fiber paper, carbon felt, and carbon nanotubes are all commonly used as electrodes in the redox flow battery⁵⁶. Since the carbon or graphitic materials have a porous structure, they can provide high electrode active surface area and good permeability. Furthermore, their properties of high electrical conductivity, chemical stability in either acidic or alkaline environments make them well suited for electrode materials.

Many combinations are possible when selecting a redox couple. Table 1.3 shows the half-cell potentials of several basic redox couples used in redox flow batteries. Selection standards for a suitable redox couple include high solubility and electrochemical stability in the electrolyte, fast electrochemical kinetics, a suitable redox potential to provide a relatively high cell voltage, and chemical stability⁷². Furthermore, to avoid hydrogen or oxygen evolution due to the crossover, the potential of anode redox species should be higher than SHE (0 V vs. SHE), and the potential of cathode redox species should be lower than the oxygen reduction potential (1.23 V vs. SHE).

Redox couple	Half-cell potential (V vs. SHE)	
Ce ³⁺ /Ce ⁴⁺	1.44	
Br ⁻ /Br ₃ ⁻	1.09	
VO ^{2+/} VO ₂ ⁺	1.00	
Fe ³⁺ /Fe ²⁺	0.77	
Sn ³⁺ /Sn ⁴⁺	0.15	
V ²⁺ /V ³⁺	-0.26	
S ₂ ²⁻ /S ₄ ²⁻	-0.27	
Ti ³⁺ /Ti ⁴⁺	-0.37	
Cr ²⁺ /Cr ³⁺	-0.41	

Table 1.3 Half-cell potentials of basic redox couples^{71,73}.

1.5 The redox fuel cell

One approach to resolve many issues associated with the reactions in fuel cells, such as slow reactions and fuel crossover, is to substitute one of the electrodes in a conventional fuel cell by a redox-species electrode to build a redox fuel fell^{74,75}, which is a hybrid of the fuel cell and redox flow battery.

llicic et al.⁷² demonstrated the replacement of the oxygen cathode by the Fe³⁺/Fe²⁺ redox couple with a carbon-based electrode in direct methanol redox fuel cells. Direct methanol redox fuel cells (DMRFCs) can be interpreted as a hybrid between a direct methanol fuel cell and a redox flow battery. The electrochemical reaction equations for the DMRFC are given by:

Anode: $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^ E = 0.016 V$	vs. SHE	(1.51)
--	---------	--------

Cathode: $Fe^{3+} + e^- \to Fe^{2+}$ $E^{\circ} = 0.769 \text{ V vs. SHE}$ (1.52)

Overall:
$$CH_3OH + 6Fe^{3+} + H_2O \rightarrow CO_2 + 6Fe^{2+} + 6H^+$$
 $E^{\circ} = 0.753 \text{ V}$ (1.53)

The key advantage of the DMRFC over the conventional DMFC is that a PGM catalyst at the cathode is not required. A three-dimensional electrode can be used since there is no triple-phase boundary constraint. 16.7 M methanol can be utilized at the anode without bringing in significant cathode issues. Other advancements, such as improving cathode kinetics and eliminating cathode flooding, are also achieved. Ilicic et al.⁷⁶ further improved the performance of the DMRFC by replacing the catholyte of FeNH₄(SO₄)₂ with Fe(ClO₄)₃. The maximum current density of the perchlorate system (79 mW/cm²) was approximately two times higher than the sulfate system (25 mW/cm²). This improvement is due to the higher solubility limit (> 3 M) of perchlorate catholyte compared with sulfate catholyte (~1 M) and the higher half-cell potential (0.83 V vs. SHE at 90 °C) compared with sulfate catholyte (0.64 V vs. SHE at 90 °C).

The fuel anode also has been substituted by a redox couple electrode to generate a redox anode fuel cell (RAFC). Kaneko et al. first patented the concept of the vanadium-oxygen redox fuel cell (VORFC) in 1992⁷⁷. The half-cell reactions are:

Anode: $V^{2+} \rightarrow V^{3+} + e^-$	<i>E</i> [°] = -0.26 V vs. SHE	(1.54)
Cathode: $0_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	<i>E</i> [°] = 1.23 V vs. SHE	(1.55)
Overall: $4V^{2+} + O_2 + 4H^+ \rightarrow 2H_2O + 4V^{3+}$	<i>E</i> °= 1.49 V	(1.56)

Menictas et al.⁷⁸ initially confirmed the feasibility and reliability of the VORFC in a 5-cell stack, which was able to be operated for over 100 hours without any degradation in the performance. Austing⁷⁹ et al. introduced a novel bidirectional two-layered cathode in a unitized vanadium/air redox fuel cell. An average discharge power density of

34.6 mW/cm² was achieved, but the sluggish oxygen reduction reaction limited the cell performance at room temperature. Considerable evolution of hydrogen at the cathode due to the oxidation of the divalent vanadium from the crossover diffusion turned out to be the most serious shortcoming of the system⁸⁰. The other challenges associated with the vanadium-oxygen redox fuel cell include the regeneration of the redox electrolyte and membrane contamination by the redox couple. A thicker membrane (Nafion 117) has been suggested to reduce the crossover of the redox couple.

1.6 Knowledge gap

Micro fuel cells must have adequate power while simultaneously maintaining the criteria of a small size and a lightweight. Although a significant amount of work has been done with micro fuel cells, it is still a design challenge to miniaturize this type of fuel cell²⁴. It is vital to increase the cell performance per volume of the fuel cell to obtain small enough fuel cells. The conventional fuel cell bipolar architecture contains a membrane electrode assembly (MEA) sandwiched between two flow field plates. Increasing the loading on the membrane does not necessarily improve the performance due to the mass transfer limitation. In micro fuel cells, since the flow field channel is small, one potential approach to enhance the performance of the fuel cell is to deposit extra anode catalyst directly on the surface of the channel walls. Different from increasing the MEA area, this approach will not affect the size of the fuel cell. The catalyst on the channel walls may fully make use of the space in the fuel cell to improve the fuel cell performance by improving the active surface area on the channel walls and also the mass transport of the reactants.

Although a few designs have employed catalyzed flow field micro channels^{30–32, 81}, based on the author's knowledge, the effect of catalyzed channel walls on the micro fuel cell performance has not been studied in any depth. In addition, to miniaturizing the fuel cell system for portable applications, it is highly desired to utilize a passive air-breathing cathode¹⁷. However, no work has combined an air-breathing cathode with the use of catalyzed anode flow field channel walls. Such a new design would have different features from the conventional bipolar design in terms of achieving a good performance. More research is required to more deeply understand the new bipolar design approach with catalyzed flow field channel walls for micro fuel cells. Some important areas of research follow:

- Evaluation of the effect of additional catalyzed flow field channels on the overall fuel cell and individual electrode performances compared with the conventional bipolar micro direct methanol fuel cell design;
- Identification of significant design parameters and operating conditions in the new designed micro fuel cell;
- The potential of applying the new catalyzed flow field channel architecture to various micro fuel cell systems with alternative electrode reactions, such as redox reactions;
- The effect of the channel dimensions on the performance of micro fuel cells with catalyzed channel walls, and the distributions of potential, current, and species within the channel.

1.7 Research objectives

The primary objective of this research project is to develop an air-breathing micro direct liquid fuel cell (µDLFC) with catalyzed flow field channel walls, and to investigate the effects of critical design parameters and operating conditions on its performance by experimental and computational approaches. This overall objective is achieved through the following sub-objectives:

- Explore the effects of the distribution and loading amount of the anode catalyst applied to the channel walls in µDMFCs on the overall and individual electrode performances according to the polarization and power density plots. Examine the effects of operating conditions of the fuel cell, such as methanol feed concentration, electrolyte concentration, fuel flow rate, and oxidant supply mode on its performance.
- Demonstrate the flexibility of the design of fuel cells with catalyzed flow field channel walls applied to other liquid-feed fuel cell system (redox anode fuel cell), and evaluate the performance of the redox anode fuel cell and determine appropriate design parameters and operating conditions.
- Develop a three-dimensional simplified computational model to simulate liquid flow, charge transfer, species mass transfer, and electrochemical reactions in the µDMFC with catalyzed flow field channel walls and evaluate the effects of the catalyst distribution, ionic conductivity, and channel dimensions on the overall fuel cell and individual electrode performances.

1.8 Thesis layout

In Chapter 1, the electrochemical theory for fuel cell design is presented. Background knowledge with respect to the designs of the micro direct methanol fuel cell and redox fuel cell is discussed.

In Chapter 2, a micro direct methanol fuel cell with an extended anode catalyst region on the channel walls is demonstrated and characterized. The µDFMC with extra anode catalyst deposited on the channel walls improves the cell performance in terms of the maximum power density but introduces a cathode depolarization. The effects of the methanol concentration, fuel flow rate, electrolyte concentration and air supply mode on the overall cell and individual electrode performances are studied and compared with that of the conventional bipolar fuel cell design.

In Chapter 3, a bipolar design with catalyzed channel walls is demonstrated in a redox fuel cell with an $FeSO_4/H_2SO_4$ electrolyte at the anode and an air-breathing oxygen cathode. The cell performance is improved significantly through the use of the graphite channel without introducing any extra cathode depolarization. The effects of the anolyte flow rate and the H_2SO_4 concentration on the RAFC performance are also studied and compared with that of the DMFC.

In Chapter 4, a three dimensional model for the µDMFC with an extended anode catalyst region on the channel walls is developed by simulating the reaction kinetics, charge transfer, mass transfer of reactants, and the parasitic current induced by

methanol crossover. The developed model is employed to examine the effects of the anode catalyst loading on the channel walls, ionic conductivity, and channel dimensions on the overall cell and individual electrode performances for fuel cells with anode catalyst both on the membrane and the channel walls, and only on the channel walls.

In Chapter 5, the overall conclusions, along with the overall significance and contributions of the research are summarized, and recommendations for further research with respect to the development of the catalyzed channel wall approach are proposed.

Chapter 2: Micro direct methanol fuel cell with a catalyzed flow field channel

2.1 Introduction

In this chapter, a novel air-breathing micro direct methanol fuel cell system with an extended active anode catalyst region is demonstrated. In contrast with the traditional bipolar MEA design, the new design includes anode catalyst on the channel walls. The cell voltage and individual electrode potential performances of the newly developed micro fuel cell are characterized and compared with that of the conventional MEA design, and critical design parameters and operating conditions are identified.

2.2 Experimental

2.2.1 Electrode preparation and fuel cell assembly

To explore the effect of different anode catalyst distributions on the performance, an airbreathing µDMFC with a single channel was developed, as shown in Figure 2.1. The dimensioned drawings of the fuel cell components are presented in Appendix A. For the sake of making the fuel cell easy to be manufactured and implemented, a graphite plate was used to make a 30 mm long fuel channel with a width of 1 mm and a depth of 1 mm. A Paasche TG-3F airbrush was used to spray the catalyst ink consisting of Pt (20 wt%) supported on Vulcan XC-72 carbon on the channel walls to obtain catalyzed walls with a 0.9 cm² geometrical area. A commercial catalyst coated Gore® membrane was used in the MEA with a Pt loading of 0.04 mg/cm² for the cathode and a Pt loading of 0.44 mg/cm² for the anode (SEM image is presented in Appendix B). The thickness of the Gore® membrane is 17 µm. A hydrophobic carbon paper (Freudenberg C3) with a micro-porous layer was employed as the cathode gas diffusion layer. A Toray carbon paper TGP-H-090 (0.28 mm) without wet proofing treatment was used for the anode diffusion layer. The Toray carbon paper was pre-treated by submerging in Millipore Milli-Q water and staying in a vacuum chamber for 30 minutes to ensure that the pores are saturated with the liquid phase. The catalyst coated membrane (CCM) and carbon paper samples were all cut by using a cutting die with a size of 3 mm × 35 mm. A thin layer of Kapton tape with an open area of 1 mm × 30 mm was used as a gasket for the anode and cathode to define a 0.3 cm^2 active geometric area.

A membrane electrode assembly (MEA) was sandwiched between the graphite channel and the gasketed cathodic current collector. Another carbon paper on the other side of the graphite plate was used to maintain the electric connection. The electrical current collectors were two 316 stainless steel plates plated with a 5 µm layer of 24K gold through electrodepositing by Acme Plating & Silver Shop Ltd. To get an air-breathing cathode, a 1 mm × 30 mm open area was created on the cathodic current collector to let the oxygen in the air diffuse to the catalyst layer. A constant air pressure of 100 psi was used to compress all the layers through a pneumatic air cylinder. The experimental system is shown in Figure 2.2. Fuel delivery was achieved by using a syringe pump (Cole Parmer 74900).



Figure 2.1 (a) Schematic diagram of the different layers of the designed fuel cell; (b) photos of different fuel cell components.



Figure 2.2 (a) Schematic diagram of the micro direct liquid fuel cell testing system; (b) photo of the fuel cell setup.

2.2.2 Fuel cell performance characterization

The μ DMFC performance was characterized by testing the overall cell and individual electrode polarization curves by using a Biologic VMP3 potentiostat in galvanostatic (current control) mode at ambient temperature and pressure ($20\pm2~^{0}$ C, 1 atm). The current densities for μ DMFCs were calculated based on the active geometric area of the CCM (0.3 cm²). A single junction silver/silver chloride reference electrode (Radiometer REF321) was employed in the individual electrode polarization measurements. It was placed in the outlet solution as shown in Figure 2.2 to avoid any catalyst poisoning due to the chloride ion from the reference electrode. The open circuit potentials were monitored as a function of time. The polarization tests were not performed until the open circuit voltage (OCV) reached a steady state when the cell voltage difference was less than 1 mV over 5 minutes. Triplicate measurements of polarization curves were conducted to determine the repeatability. The voltage difference between different measurements at each current density was less than 10 mV for all the tests.

Electrochemical Impedance Spectroscopy (EIS) was used to measure the fuel cell resistance twice under the open circuit condition. The impedance spectra were collected by a Biologic VMP3 at open circuit voltage by applying an AC amplitude of 10 mV in a frequency range from 0.01 Hz to1000 kHz.

2.2.3 Design parameters

Three designs consisting with various anode catalyst distributions (Figure 2.3) were studied. Anode catalyst was only deposited on the channel walls for design (a); anode

catalyst was deposited only on the membrane for design (b); anode catalyst was coated both on the membrane and the channel walls for design (c).



Figure 2.3 Cross-sectional view of designs with different anode catalyst distributions.

Table 2.1 illustrates the Pt loadings that were applied to the anode for different designs. The performance of design (c) was tested under two different anode catalyst loadings on the channel walls.

Table 2.1 Catalyst loadings of three different designs.

	Cathode Pt, mg/cm ²	Anode Pt on CCM, mg/cm ²	Anode Pt on channel walls, mg/cm ²
Wall only	0.04 <u>+</u> 0.01	0	0.20 <u>+</u> 0.015
CCM only	0.04 <u>±</u> 0.01	0.44 <u>±</u> 0.01	0
CCM & Wall	0.04 <u>±</u> 0.01	0.44 <u>+</u> 0.01	0.20/0.50±0.015

2.2.4 Operating conditions

The operating conditions of the baseline case for the fuel cell with an extended catalyst region on the channel walls are shown in Table 2.2.
Table 2.2	Operating	conditions f	for the	baseline	case.
-----------	-----------	--------------	---------	----------	-------

Methanol concentration	Sulfuric acid concentration	Fuel flow rate	Air supply mode	Temperature
1 M	0.1 M	0.1 ml/min	Air-breathing	Room <i>T</i> (20±2 ⁰ C)

Different from the conventional micro DMFCs, sulfuric acid was added to the methanol solution as a proton transport medium to improve the proton conductivity of the solution⁸¹ since the extended anode catalyst region on the channel walls was not in contact with the membrane. It would be ideal to operate an air-breathing fuel cell at room temperature to miniaturize the μ DMFC, therefore all the measurements were done under ambient conditions.

Methanol concentration, sulfuric acid concentration, fuel flow rate and air supply mode can significantly impact the performance of fuel cells with extra anode catalyst on the channel walls. The effects of these parameters on the overall cell and individual electrode performances were tested for the fuel cell design (c). The tested operating conditions are shown in Table 2.3. When evaluating a certain parameter, all the other parameters were maintained under the baseline case. To examine the different features in the fuel cells with anode catalyst on the channel walls with the conventional fuel cell with just a CCM, design (b) was also tested under the same conditions. The design (a) was not studied due to its low performance at the conditions of the baseline case, but this design was further investigated through the modeling method, which will be presented in Chapter 4. The baseline case and all the tested conditions were chosen according to both the preliminary testing results and the proper values reported in the literature concerning micro DMFCs^{28,40}.

Table 2.3 Operatin	g conditions fo	r the fuel cell	designs (b	o) and (c).
--------------------	-----------------	-----------------	------------	-------------

Operating condition	Tested case
Methanol concentration, M	0.1, 1, 5
Sulfuric acid concentration, M	0, 0.01, 0.1, 0.5
Fuel flow rate, ml/min	0.001, 0.01, 0.1,0.5
Air supply mode	Air-breathing, Air-blowing

2.3 Results and discussion

The effects of the important design parameters and operating conditions on the performance of µDMFCs with extra anode catalyst on the channel walls were discussed and compared with the typical bipolar design.

2.3.1 Design parameters

The tested design parameters include the anode catalyst distribution and the anode catalyst loading on the channel walls. The comparison between fuel cells with different anode catalyst distribution can help to better explain the effect of catalyzed channel walls on the micro fuel cell performance. The catalyst loading is a crucial parameter affecting the fuel cell performance. To determine a proper catalyst loading, the effect of anode catalyst loading on the channel walls on the fuel cell performance was studied for design (c).

2.3.1.1 Anode catalyst distribution



Figure 2.4 Polarization and power density curves for µDMFCs with different anode catalyst distributions at ambient temperature and pressure and 1 M methanol/0.1 M sulfuric acid at a flow rate of 0.1 ml/min.

A comparison of fuel cell performance of μ DMFCs with different anode catalyst distributions at room temperature and pressure is shown in Figure 2.4. The open circuit potentials are less than 0.3 V, but the expected OCV for typical DMFCs is 0.5-0.7 V⁸². The main reason for the low OCV is due to the mixed potential on the cathode induced by the reaction of the methanol crossing over from the anode.

It can be seen that the fuel cell with anode catalyst deposited both on the channel walls and the membrane has the best cell performance. The extra anode catalyst on the channel walls improves the maximum power density by 20%. This improvement in the cell performance is mainly due to the increase of the active surface area on the channel walls for the methanol electro-oxidation reaction. The fuel cell with anode catalyst only deposited on the channel walls has a much lower open circuit potential and a steeper slope than the other two designs. This poor performance is because of a higher methanol crossover flux when there is no anode catalyst layer on the membrane, and also a higher ionic resistance at the anode since the protons generated on the channel walls need to travel a longer distance to the cathode than the protons generated on the CCM.

According to the measured conductivity (3.684 ± 0.004 S/m) of 1 M methanol/0.1 M sulfuric acid electrolyte, the ionic resistance of the acidic solution is $12.9 \pm 0.1 \Omega$ for protons generated on the top wall (furthest away from the membrane). This resistance is much higher than the cell resistance at the OCV for fuel cells with different anode catalyst distributions as shown in Table 2.4. The cell resistance was determined by the intercept at high frequency on the real axis in the Nyquist plots of the EIS measurements (All the impedance spectra are presented in Appendix C). As we expected, the cell resistances were similar for the three designs because the total cell resistances of the electrodes, backing diffusion layers, and current collector layers, and the contact resistances between each of the components^{83,84}. The increased ionic resistance due to the longer proton transfer distance for the fuel cell with anode catalyst only on the channel walls is not included in this total cell resistance.

Anode catalyst distribution	Cell resistance at the OCV, $\boldsymbol{\Omega}$
Wall only	1.09±0.12
CCM only	0.94±0.03
CCM & Wall	1.07±0.05

Table 2.4 Cell resistances for µDMFCs with different anode catalyst distributions.



Figure 2.5 Individual electrode polarization curves for µDMFCs with different anode catalyst distributions.

The cell polarization curves only show the total loss mechanisms, containing both the anode and cathode information. However, it is difficult to distinguish the individual contributions due to the superposition of the behaviors at both the anode and cathode. An Ag/AgCl reference electrode was applied to measure the individual electrode potentials. Figure 2.5 shows the individual electrode potentials for the fuel cells with different anode catalyst distributions. The results show that the µDMFC with anode catalyst deposited on both the channel walls and the membrane has the best anode

performance. The improved anode performance is reflected in the overall cell polarization plots. The result indicates the fuel cell performance is limited by the charge transfer kinetics at the anode. According to the Nernst equation of the anode reaction, as shown in equation 2.1, the anode equilibrium potential reduces with an increase in local methanol activity (effective concentration). The decreased anode potential at the OCV is likely due to the increased methanol concentration at the active sites of the anode catalyst layer on the channel walls.

$$E_{e,a} = E^o - \frac{RT}{6F} ln \left(\frac{a_{methanol}}{a_{co_2} a_{H^+}^6} \right)$$
(2.1)

Even though the total Pt catalyst loading on the channel walls (0.2 $mg_{Pt}/cm^2 \times 0.9$ $cm^2=0.18 mg_{Pt}$) is higher than the loading (0.44 $mg_{Pt}/cm^2 \times 0.3 cm^2=0.132 mg_{Pt}$) on the membrane, the fuel cell with anode catalyst only deposited on the channel walls has a higher anode overpotential than the conventional design. This result indicates that the spray-deposited anode catalyst on the channel walls has a lower activity.

The individual electrode polarization curves also show that the fuel cell with anode catalyst deposited both on the channel walls and the membrane has a lower cathode potential than the fuel cell with anode catalyst only on the membrane. The two designs have the same anode catalyst layer on the membrane. Therefore the diffusion flux of the methanol crossover should be similar at the OCV, and the cathode performance drop is not due to the methanol crossover but a reflection of the increased ohmic loss. For the fuel cell with extra anode catalyst on the channel walls, a certain number of protons are generated from the channel walls. As discussed above, the protons

generated from the anode on the walls need to travel a longer distance than the protons generated at the membrane anode, leading to an increased resistance in proton transfer. For the fuel cell with anode catalyst only deposited on the channel walls, the cathode potential is significantly low due to the increase of the fuel crossover flux and the ionic resistance.

2.3.1.2 Anode catalyst loading on the channel walls

If increasing the anode catalyst loading on the membrane, the active surface for the methanol oxidation reaction may increase up to a certain point. However, the increased thickness of the catalyst layer may also at some point result in mass transport limitations for methanol and CO₂⁵³. So at some point increasing the loading of the catalyst on the membrane may not improve the cell performance. To study the effect of the catalyst loading on the channel walls and determine a proper loading to enhance the performance, fuel cells with a CCM, and 0.2 mg/cm² or 0.5 mg/cm² Pt on the channel walls were evaluated. Figure 2.6 shows the fuel cell performance with two different loadings of anode catalyst on the channel walls. The increased catalyst loading does not improve the overall fuel cell performance as expected. It can be seen from Figure 2.7 that the increased catalyst loading on the walls enhances the anode performance, but the cathode performance declines at the same time.



Figure 2.6 Polarization and power density curves for µDMFCs with anode catalyst deposited both on the membrane and channel walls for different loadings of Pt on the channel walls at ambient temperature and pressure and 1 M methanol/0.1 M sulfuric acid at a flow rate of 0.1 ml/min.



Figure 2.7 Individual electrode polarization curves for µDMFCs with anode catalyst deposited both on the membrane and channel walls for different loadings of Pt on the channel walls.

The total cell resistances at the OCV and voltage losses due to this resistance at 15 mA/cm² for fuel cells with different anode catalyst loadings are shown in Table 2.5. Even though increasing catalyst loading on the channel walls increases the cell resistance, the difference of the voltage loss at 15 mA/cm² is only about 3.7 mV (~45 mV of total actual cathode potential drop). The change in cell resistance is not the main source of the drop in cathode performance. As a result of the increase of the catalyst loading on the channel walls, the proportion of the protons generated near the membrane goes down. The protons produced on the channel walls have to transport through the acidic fuel to reach the membrane and also the fuel crossover increases due to the increase of the concentration gradient in the membrane. The increase of the ionic resistance and parasitic power losses due to the methanol oxidation at the cathode lead to a degradation of the cathode performance.

Table 2.5 Cell resistances and voltage losses for μ DMFCs with different anode catalyst loadings on the channel walls.

Fuel cell design	Cell resistance at the OCV, Ω	Voltage loss at 15 mA/cm ² , mV
CCM and 0.2 mg/cm ² Pt on channel walls	2.19 <u>+</u> 0.04	9.8 <u>+</u> 0.2
CCM and 0.5 mg/cm ² Pt on channel walls	3.00 <u>+</u> 0.15	13.5 <u>+</u> 0.7

2.3.2 Operating conditions

The impact of methanol concentration, sulfuric acid concentration, fuel flow rate and the air supply mode on the cell performance were evaluated mainly because these parameters can have an impact on the fuel cell performance by affecting the mass transfer of the reactants and products, and the proton transfer.

2.3.2.1 Effect of methanol concentration

The methanol concentration mainly impacts two behaviors, i) the coverage of the active sites on the anode side, and ii) the methanol concentration gradient in the membrane related to the fuel crossover on the cathode side²⁸. The choice of methanol concentration requires the consideration of the balance between the effects of the reaction kinetics and fuel crossover. Figure 2.8 shows the cell polarization curves of the micro fuel cell with a CCM and a 0.2 mg/cm² Pt loading on the channel walls for three different methanol concentrations at ambient temperature and pressure. An acidic fuel solution of methanol mixed with 0.1 M sulfuric acid was fed to the cell at a flow rate of 0.1 ml/min. It can be seen in Figure 2.8 that the performance at 1 M methanol is the best among all the testing methanol concentrations. It achieves a maximum power density of 1.37 ± 0.03 mW/cm². The best performance was also obtained at 1 M methanol in other researches with regard to air-breathing micro DMFCs^{54,85}. The performance drops when the methanol concentration is increased to 5 M. This decrease is expected since a higher methanol concentration can improve the methanol mass transfer and provide sufficient reactant to the catalyst sites for the electrochemical reaction, but high methanol concentration results in a high rate of fuel crossover to the cathode side and generates a mixed potential on the cathode. The performance is the worst when the concentration is only 0.1 M, and the performance loss is noticeable even at very low current densities. This phenomenon can be explained by the limitation of a shortage of methanol at the anode active sites to perform the reaction.



Figure 2.8 Polarization and power density curves for µDMFCs with anode catalyst deposited both on the membrane and channel walls at ambient temperature and pressure and different concentrations of methanol/0.1 M sulfuric acid at a flow rate of 0.1 ml/min.



Figure 2.9 Polarization and power density curves for µDMFCs with anode catalyst deposited only on the membrane at ambient temperature and pressure and different concentrations of methanol/0.1 M sulfuric acid at a flow rate of 0.1 ml/min.

Figure 2.9 shows the cell polarization results of fuel cells with a CCM only (no channel catalyst) at the three different methanol concentrations. Compared with the results of fuel cells in Figure 2.8, at methanol concentration of 0.1 M, 1 M and 5 M, the fuel cell with the extra anode catalyst on the channel walls increases the maximum power density by 22%, 12%, and 8%, and increases the current density at a cell voltage of 0.02 V by 85%, 20%, and 12%, respectively. The anode catalyst on the channel walls improves the current density at lower cell voltage and maximum power density more significantly at low methanol concentration. At 0.1 M methanol, the supply of methanol significantly limits the overall performance at higher current densities, and the catalyst layer on the membrane is mainly starved of methanol. Under the fuel starvation condition, adding catalyst loading on the membrane cannot increase the current density as fresh reactant cannot be delivered fast enough to the catalyst surface. However, the additional catalyst on the channel walls can increase the current significantly. The catalyst layer on the walls increases the geometric surface area of the anode and the reactant methanol can reach the catalyst layer more easily since there is no carbon paper diffusion layer on the catalyst layer. Thus, the micro fuel cells with anode catalyst on the channel walls have a better mass transport of methanol in terms of diffusion, which allows the fuel cells to be operated at a lower optimal methanol concentration than the fuel cell with a CCM only to get the best performance.



Figure 2.10 Individual electrode polarization curves for µDMFCs with anode catalyst deposited both on the membrane and channel walls under different methanol concentrations.



Figure 2.11 Individual electrode polarization curves for µDMFCs with anode catalyst deposited only on the membrane under different methanol concentrations

Figure 2.10 and Figure 2.11 show the effect of methanol concentration on the individual electrode potentials. As can be seen from the figures, the increase of the methanol concentration improves the anode performance but drops the cathode potentials. This is consistent with the conclusions from the overall cell performance. The increase of the methanol concentration can improve the methanol mass transport so that it increases the anode performance, but the higher methanol concentration degrades the cathode performance due to the mixed potential produced by the crossover of fuel to the cathode. It is interesting to note that the anode performance of the fuel cell with catalyst on the channel walls is less significantly impacted by the methanol concentration than the fuel cell with a CCM only.

2.3.2.2 Effect of anode flow rate

The anode flow rate is an important parameter since it generally affects the supply of the methanol to the catalyst layer and the removal of the carbon dioxide⁵⁶. Figure 2.12 shows the cell polarization curves of fuel cells with a CCM and a 0.2 mg/cm² Pt loading on the channel walls at four different flow rates of an acidic methanol solution (1 M methanol/0.1 M sulfuric acid) at ambient temperature and pressure. It can be seen that the cell performance improves with an increase in the flow rate from 0.001 ml/min to 0.1 ml/min. The fuel cell performance is only marginally improved when the fuel flow rate is higher than 0.1 ml/min. The performance improvement with the increase of the flow rate is likely due to an increase of methanol supply rate and a more efficient removal of CO₂.



Figure 2.12 Polarization and power density curves for µDMFCs with anode catalyst deposited both on the membrane and channel walls at ambient temperature and pressure and 1 M methanol/0.1 M sulfuric acid solution at different flow rates.



Figure 2.13 Polarization and power density curves for µDMFCs with anode catalyst deposited on the membrane only at ambient temperature and pressure and 1 M methanol/0.1 M sulfuric acid solution at different flow rates.

As can be seen from Figure 2.13, the performance of fuel cells with a CCM alone does not change significantly with the increase of the fuel flow rate from 0.01 ml/min to 0.5 ml/min. When the flow rate is only 0.001 ml/min, an obvious performance drop can be found at the higher current density region, indicating a mass transport limitation of methanol. The current density at 0.01 V of the fuel cell with additional anode catalyst on the channel walls in Figure 2.12 increases by 13% at a low flow rate (0.001 ml/min) compared to the fuel cell performance in Figure 2.13. Therefore, fuel cells with anode catalyst on the channel walls have better mass transfer of methanol in terms of convection.



Figure 2.14 Individual electrode polarization curves for µDMFCs with anode catalyst deposited both on the membrane and channel walls at different flow rates of 1 M methanol/0.1 M sulfuric acid solution.



Figure 2.15 Individual electrode polarization curves for µDMFCs with anode catalyst deposited on the membrane only at different flow rates of 1 M methanol/0.1 M sulfuric acid solution.

The effect of flow rate of methanol solution on individual electrode potentials is shown in Figure 2.14 and Figure 2.15. For fuel cells with anode catalyst on the channel walls, no evident improvement in the anode performance is found when the flow rate is higher than 0.01 ml/min, which means the mass transfer of methanol was not a limiting factor at flow rates beyond 0.01 ml/min. When reducing the flow rate to 0.001 ml/min, the anode performance only slightly decreases, while for the fuel cell with a CCM only, the anode performance drop is evident in the higher current density region. The methanol has better access to the active sites of the catalyst layer on the channel walls than to the catalyst layer on the membrane in the conventional bipolar design. The fuel cell with extra catalyst on the channel walls has a higher current density at a lower potential region, allowing the fuel cell to be operated at a lower flow rate even a passive fuel supply mode (no external accessories for delivering fuels). However, the individual

cathode performance declines when the flow rate is very slow for the fuel cells with catalyzed walls. This change may due to the insufficient removal of the CO_2 in both the diffusion layer and the channel at a very low fuel flow rate. The CO_2 in the system inhibits the transfer of the protons generated by the anode on the channel walls, leading to a rise in the cathode overpotential. On the contrary, the cathode performance improves at the flow rate of 0.001 ml/min for the fuel cell without catalyst on the channel walls. As the catalyst is only on the membrane, CO_2 stuck in both the diffusion layer and the channel does not affect the proton transfer through the membrane. Thus, the cathode potential increases as a result of the reduction of fuel crossover.

2.3.2.3 Effect of sulfuric acid concentration

The extended anode catalyst region on the channel walls is not in contact with the membrane, thus sulfuric acid was added to the methanol solution as a proton transport medium to enhance the proton conductivity of the solution. Figure 2.16 shows the effect of the sulfuric acid concentration on the performance of fuel cells with a CCM and a 0.2 mg/cm² Pt loading on the channel walls at ambient temperature and pressure. An acidic fuel solution of 1 M methanol mixed with sulfuric acid was fed to the cell at a flow rate of 0.2 ml/min. The cell resistances at the OCV and the voltage losses due to this resistance at 15 mA/cm² for fuel cells with different acid concentrations are shown in Table 2.6. The cell resistance decreases with an increase of the acid concentrations, indicating the acidic solution can benefit the proton transfer through the membrane. According to the voltage losses due to the cell resistance at 15 mA/cm² as shown in

Table 2.6, the difference in this ohmic loss is not the main reason for the trend of the fuel cell performance in Figure 2.16.



Figure 2.16 Polarization and power density curves for µDMFCs with anode catalyst deposited both on the membrane and channel walls at ambient temperature and pressure and different concentrations of sulfuric acid/1 M methanol at a flow rate of 0.2 ml/min.

Table 2.6 Cell resistances and voltage losses for µDMFCs with anode catalyst both on t	the
membrane and the channel walls under different sulfuric acid concentrations.	

Sulfuric acid concentration, M	Cell resistance at the OCV, Ω	Voltage loss at 15 mA/cm ² , mV
0	2.79±0.03	12.6±0.2
0.01	2.18±0.03	9.8±0.2
0.1	1.91±0.03	8.6± 0.2
0.5	1.62±0.02	7.3±0.1

As shown in Figure 2.16 the maximum current density obtained for the fuel with 0.01 M sulfuric acid is slightly higher than the fuel without acid. This is expected because the acid in the fuel increases the proton conductivity. No significant change is found when

changing the acid concentration from 0.01 M to 0.1 M. When increasing the acid concentration to 0.5 M, in spite of the improvement in the ionic conductivity, the overall cell performance slightly drops. This degradation can be explained by a decrease in the Pt active sites due to blockage from the bisulfate anion⁸⁶. Also, as the sulfuric acid concentration is increased, the number of active sites that are poisoned by the intermediates of the methanol-oxidation reaction increases and the coverage of the active Pt-OH_{ad} species to oxidize the methanol is lowered⁸⁷.

For the conventional bipolar fuel cell without catalyst on the channel walls, as shown in Figure 2.17, the addition of the acid does not benefit the cell performance. The cell resistances at the OCV and voltage losses due to this resistance at 15 mA/cm² are shown in Table 2.7. The trend of cell resistances with the acid concentrations is the same as the fuel cell with anode catalyst both on the membrane and the channel walls, but no fuel cell performance improvement is observed with a reduction of the cell resistance. Although the utilization of acidic methanol solution can improve the proton conductivity, the reduced ohmic loss is less than the extra kinetic loss of the anode due to the acidic fuel. Therefore the overall cell performance drops with an increase of the acid concentration.



Figure 2.17 Polarization and power density curves for μ DMFCs with anode catalyst deposited on the membrane only at ambient temperature and pressure and different concentrations of sulfuric acid/1 M methanol at a flow rate of 0.2 ml/min.

Table 2.7 Cell resistances and voltage losses for μ DMFCs with anode catalyst only on the membrane under different sulfuric acid concentrations.

Sulfuric acid concentration,	Cell resistance at the	Voltage loss at 15
Μ	OCV, Ω	mA/cm², mV
0	3.19±0.05	14.4±0.3
0.01	2.66±0.07	12.0±0.4
0.1	2.23±0.03	10.0± 0.2
0.5	1.78±0.05	8.0± 0.3



Figure 2.18 Individual electrode polarization curves for µDMFCs with anode catalyst deposited both on the membrane and channel walls under different sulfuric acid concentrations.



Figure 2.19 Individual electrode polarization curves for µDMFCs with anode catalyst deposited on the membrane only under different sulfuric acid concentrations.

Figure 2.18 and Figure 2.19 show the effect of the sulfuric acid concentration on the individual electrode potentials. It can be seen that the anode and cathode potentials rise significantly with an increase of the acid concentration for both fuel cell designs. The potential changes at the open circuit condition are mainly due to the changes in the equilibrium electrode potential. The proton concentration on the electrode surface can affect the equilibrium individual electrode potentials since the protons are the product of the anode reaction and the reactant of the cathode reaction. Equations 2.1 and 2.2 show the Nernst equations used to calculate the equilibrium potentials of the anode and cathode with an increase of the proton activity a_{H^+} .

$$E_{e,a} = E^o - \frac{RT}{6F} ln \left(\frac{a_{methanol}}{a_{co_2} a_{H^+}^6} \right)$$
(2.1)

$$E_{e,c} = E^o - \frac{RT}{4F} ln\left(\frac{1}{a_{o_2}a_{H^+}^4}\right)$$
(2.2)

Table 2.8 Measured E_a at the OCV and calculated $E_{e,a}$ under different sulfuric acid concentrations.

$C_{H_2SO_4}$, M	<i>E_a</i> (CCM & wall), V vs. SHE	<i>E_a</i> (CCM only), V vs. SHE	<i>E_{e,a}</i> V vs. SHE
0.01	0.439±0.002	0.407±0.001	-0.094
0.1	0.443 ± 0.002	0.43± 0.003	-0.048
0.5	0.473±0.003	0.465± 0.003	-0.016

Table 2.8 shows the comparison of the effect of the sulfuric acid concentration on the measured anode potential E_a at the OCV and the calculated anode equilibrium potential $E_{e,a}$ obtained by assuming that the activities of methanol and carbon dioxide are both 1, and the local proton activity at the anode is equal to the proton activity in the bulk

solution. According to equation 2.3, the proton activity can be determined by the pH value of the acidic methanol solution⁸⁸. The measured pH values for 1 M methanol solutions with 0.01 M, 0.1 M and 0.5 M sulfuric acid are 1.89 ± 0.01 , 1.10 ± 0.01 , and 0.55 ± 0.01 , respectively.

$$a_{H^+} = 10^{-pH} \tag{2.3}$$

The trend of the measured E_a with the acid concentration is similar to the tend of the calculated $E_{e,a}$. Therefore, the differences of E_a at the OCV is likely due to the changes of $E_{e,a}$ under different sulfuric acid concentrations.

The anode kinetic losses that have been explained previously are the other reason for the anode degradation with the increase of the acid concentration. The proton conductivity is the other factor that can lead to a rise in cathode potential, especially in the higher current density region for fuel cells with anode catalyst on the channel walls.

2.3.2.4 Effect of air supply mode

The air supply mode is another crucial operating condition in the µDMFC by affecting the oxygen reduction reaction and the proton conductivity. To determine whether oxygen supplied by the natural convection and diffusion of the air is sufficient for the operation, air at flow rates of 0.120 L/min and 6 L/min was blown to the cathode side of the fuel cell. Figure 2.20 shows the results of polarization curves of fuel cells with the different air supply modes. The air-blowing mode performs worse than the passive air-breathing mode, and the performance drops as the air flow rate increases. This result

contradicts our expectation that a higher air flow rate should produce a better performance due to improved oxygen mass transfer. Therefore, the passive airbreathing mode can supply sufficient oxygen when the current density is below 30 mA/cm². This is consistent with the literature data where air-breathing fuel cells appear to show an oxygen mass transfer limitation when the current density is higher than 70 mA/cm², as shown by Li et al⁶⁰. The cell resistances at the OCV for fuel cells with different air supply modes are shown in Table 2.9. The cell resistances are very similar for fuel cells operated under different air supply modes, so the performance difference in Figure 2.20 is not due to the resistance change in the membrane.



Figure 2.20 Polarization curves for μ DMFCs with anode catalyst deposited both on the membrane and channel walls under different air supply modes at ambient temperature and 1 M methanol/0.1 M sulfuric acid at a flow rate of 0.1 ml/min.

Table 2.9 Cell resistances for µDMFCs with different air supply modes.

Air supply mode	Cell resistance at the OCV, $\boldsymbol{\Omega}$
Air-breathing	0.98 <u>+</u> 0.07
Air-blowing-low flow rate	0.91 <u>+</u> 0.04
Air-blowing-high flow rate	1.11 <u>+</u> 0.22

Figure 2.21 shows the effect of the air supply mode on the individual electrode performance. It can be seen that the cathode potentials drop as the air flow rate increases, while the anode potentials do not change in any obvious way. The cathode potentials decrease with the air flow since the forced air removes water from the ionomers at the cathode, which results in drying and a lower localized ionic conductivity in the cathode catalyst layer.



Figure 2.21 Individual electrode polarization curves for µDMFCs with anode catalyst deposited both on the membrane and channel walls under different air supply modes.

2.4 Summary

- The µDMFC with extra anode catalyst deposited on the channel walls improved the anode and overall cell performances. However, the contribution of the current from the anode catalyst on the walls also increased the total ohmic loss by increasing the distance of proton transfer at the anode.
- Increasing the catalyst Pt loading on the channel walls from 0.2 mg/cm² to 0.5 mg/cm² did not improve the fuel cell performance due to the increased ohmic loss.
- The current density at a lower cell voltage (0.02 V) was larger for the fuel cell with extra catalyst on the channel walls compared to the conventional fuel cell design with a CCM only under the operating conditions of a very low methanol concentration (0.1 M) or a very low fuel flow rate (0.001 ml/min). Therefore, the methanol has better access to the catalyst active sites on the channel walls than to the catalyst layer on the membrane in the conventional bipolar design.
- For the fuel cell with extra catalyst on the channel walls, adding 0.01~0.1M sulfuric acid in the fuel solution to promote the proton transfer could improve the fuel cell performance. However, acidic fuel cannot show benefit for the conventional fuel cell design.
- When the operating current density was less than 30 mA/cm², the passive airbreathing mode could supply sufficient oxygen to the cathode. The ionic conductivity of the cathode catalyst layer was a limiting factor to the fuel cell performance.

Chapter 3: Micro redox anode fuel cell with catalyzed flow field channel

3.1 Introduction

The performance of the DMFC is limited by the slow reactions at the anode and cathode. methanol crossover, and water flooding at the cathode. To resolve the issues associated with the reactions in DMFCs, one approach is to substitute the cathode in a conventional DMFC by a redox-species electrode⁷² to form a redox fuel fell, which is a hybrid of a fuel cell and a redox battery. A Fe²⁺/Fe³⁺ redox couple is one of the examples that can be used to replace the oxygen cathode. Only a carbon electrode is required at the cathode for the reaction of the Fe^{2+}/Fe^{3+} couple⁸⁹, instead of platinum group metal (PGM) catalysts. Compared with the conventional DMFC, a mixed potential will not be created on the cathode since the methanol oxidation reaction will not occur on the carbon-based electrode. Thus, high methanol concentration can be used at the anode, and there is no cathode flooding due to the application of the liquid-form electrolyte. However, redox couples also bring in some challenges, such as the regeneration of the redox couple, contamination of the membrane, and crossover of the redox couple. Since the oxidant of the redox couple gains electrons during the process of cell discharge, the reduced redox species needs to be regenerated back to its oxidizing form. For the regeneration of the redox couple, the conventional approaches include chemical^{90,91}, electrochemical⁹² and biochemical^{93,94} regeneration in an external reactor, which impacts the simplicity and efficiency of the overall fuel cell system. One in-situ regeneration method is to use an air cathode to regenerate the redox couple at the anode⁹⁵. We call this regeneration cell as a redox anode fuel cell (RAFC), in which

power is also produced during the regeneration. The electrochemical reactions for the Fe^{2+}/Fe^{3+} RAFC are:

Anode:
$$Fe^{2+} \to Fe^{3+} + e^{-}$$
 $E^{o} = 0.77 \text{ V vs. SHE}$ (3.1)

Cathode:
$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$
 $E^o = 1.229 \text{ V vs. SHE}$ (3.2)

Overall: $O_2 + 4Fe^{2+} + 4H^+ \rightarrow 2H_2O + 4Fe^{3+}$ $E^o = 0.459 \text{ V}$ (3.3)

In this chapter, the bipolar design with catalyzed channel walls is demonstrated and characterized in a Fe²⁺/Fe³⁺ μ RAFC. The effects of the catalyzed channel walls and the thickness of the anode layer on the overall cell and individual performances are characterized, and the crucial operating conditions are identified. In addition, the effect of the catalyzed anode channel walls in the μ RAFC on the overall cell and individual electrode performances is compared with that in the μ DMFC. Unlike the μ DMFC, no protons are generated through the reaction of the redox couple at the anode, and the protons in the cathode reaction must be provided from the other supporting acid electrolyte. The comparison between the performances of the μ DMFC and μ RAFC provides a better understanding of the effects of proton distribution and transfer on the performance of the fuel cell with catalyzed channel walls.

3.2 Experimental

3.2.1 Electrode preparation and cell assembly

Since a Fe²⁺/Fe³⁺ redox couple has been shown to exhibit a good electrochemical activity on a carbon-based electrode⁸⁹, channel walls made in a graphite plate directly served as an anode without any catalyst deposition. To provide a comparison with

conventional fuel cell design, a Toray TGPH090 carbon paper (280 µm) without wetproofing treatment was put on the membrane as the anode. To improve the wetting of the ferrous sulfate solution in the anode, the graphite channel plate and carbon papers were submerged in a solution of 1 M nitric acid at 90°C for an hour at first, and then boiled and rinsed in Millipore Milli-Q water. This treatment oxidizes the carbon surface to generate more surface oxygen functional groups, such as carboxyl, alcoholic, ketone and ester groups⁹⁶. These oxygen groups result in an improvement in porosity and a reduction of hydrophobicity for the electrode material^{97,98}, providing more active sites and effective electrode area to promote the electron transfer reaction⁶⁹. Before assembly, the Toray paper and graphite plate were submerged in Millipore Milli-Q water and then placed in a vacuum chamber for 30 minutes to ensure that the pores were saturated with the liquid phase. After the saturation of water, the anodes were rapidly transferred into a 1 M H₂SO₄ solution to provide an uptake of the electrolyte into the electrodes. A commercial one-side catalyst coated Gore® membrane was used for the cathode with a catalyst loading of 0.4 mg/cm² Pt. A piece of PTFE treated carbon paper (Freudenberg C3) with a thickness of 290 µm was used as the gas diffusion layer for air. The CCM and carbon paper samples were all cut by using a cutting die with dimensions of 3 mm × 35 mm.

Figure 3.1 shows the cross-sectional view of the redox anode fuel cell. The configuration of the RAFC is similar to the DMFC with the only difference being the absence of Pt catalyst layers at the anode. To assemble the RAFC, a thin layer of Kapton tape with an open area of 1 mm \times 30 mm was covered on the non-catalyst side

74

of the membrane defining a 0.3 cm² active area for the proton transfer. The size of the flow channel was the same as the one used in the DMFC. The same electrical current collectors and holders as used in the μ DMFC were employed for the μ RAFC. A constant air pressure of 100 psi was applied to pressurize all the layers through a pneumatic air cylinder.



Figure 3.1 A cross-sectional view of the redox anode fuel cell (RAFC).

3.2.2 µRAFC performance characterization

The performance of the RAFC was evaluated by measuring the cell and individual electrode polarization curves using a Biologic VMP3 potentiostat in a galvanostatic mode at room temperature (20 ± 2 °C) and ambient pressure. The current densities for µRAFCs were calculated based on the active geometrical area of the membrane (0.3 cm²). An Ag/AgCl reference electrode placed in the anode outlet solution as shown in Figure 2.2 was used for the individual electrode potential measurement to distinguish the individual electrode limitations. The results of the redox fuel cell tests were used to identify proper design parameters and operating conditions that yield enhanced cell performance. The open circuit potentials were monitored as a function of time. The

polarization tests were not performed until the OCV reached a steady state when the cell voltage difference was less than 1 mV in 5 min. Triplicate measurements of polarization curves were conducted to determine the repeatability. The voltage differences at given currents were less than 10 mV in all the tests.

Electrochemical impedance spectroscopy (EIS) was used to measure the cell resistance twice under the open circuit condition. The impedance spectra were collected through applying an AC amplitude of 10 mV in a frequency range from 0.01 Hz to1000 kHz by the Biologic VMP3.

3.2.3 Experimental design and operating conditions

Since the walls of the graphite channel can directly provide a high electrochemical activity for the reaction of the Fe^{2+}/Fe^{3+} redox couple, to evaluate the effect of catalyzed channel walls on the overall cell and individual electrode performances in the µRAFC, a piece of PTFE plate with the same channel size as the graphite channel was used as an inactive channel in the µRAFC for comparison. Also, the performance of µRAFCs with different numbers of carbon paper layers on the membrane (similar parameter as the anode catalyst loading) was characterized.

The reaction of the redox couple at the anode cannot produce protons, so an acid electrolyte must be employed. The anolyte consisted of ferrous sulfate mixed with the sulfuric acid solution. Due to the limited solubility of $FeSO_4$ in water, the concentration of $FeSO_4$ was kept at 1 M for all the measurements. The impact of anolyte flow rate on the

76

overall and individual electrode performances of the RAFCs was studied at flow rates of 0.1 ml/min, 1 ml/min, 2 ml/min, and 5 ml/min. The electrolyte solution was fed by a syringe pump (Cole Parmer 74900). The effect of acid concentration on the overall and individual electrode performances of the RAFCs was studied at H_2SO_4 concentrations of 0.5 M, 1 M, and 2 M.

3.3 Results and discussion

To demonstrate the flexibility of the design with catalyzed channel walls in the redox anode fuel cell and further understand the features of this design, the effects of the crucial design parameters and operating conditions on the performance of the redox anode fuel cells were evaluated.

3.3.1 Design parameters

The distribution and thickness of the electrode are important parameters affecting the electro-reaction rate at the anode. The performance of μ RAFCs with active or inactive channel walls for the redox reaction was evaluated. The effect of the anode thickness was examined by characterizing the performance of RAFCs with different numbers of carbon paper layers on the membrane.

3.3.1.1 Anode distribution

The effect of the catalyzed channel walls on the performance of the µRAFC at room temperature and pressure is shown in Figure 3.2 by comparing two different designs. Both of the designs have one layer of Toray TGPH090 carbon paper on the membrane

77

as an anode. The fuel cell with a graphite channel has anode layers on both the membrane and the channel walls, while the fuel cell with a PTFE channel has an anode only on the membrane. The open circuit potentials of the RAFCs are less than 0.25 V (expected value is about 0.46 V), indicating redox couple crossover yields a mixed potential on the cathode in the RAFC. The RAFC with an anode only on the membrane has a much lower open circuit potential and a steeper cell potential slope than the design with a graphite channel. The catalyzed anode channel walls improved the performance by 281% in terms of maximum power density.



Figure 3.2 The polarization and power density curves for μ RAFCs with different channel materials at ambient temperature and pressure and 1 M FeSO₄/1 M H₂SO₄ at a flow rate of 0.1 ml/min.

The total cell resistances at the OCV for RAFCs with different channel material are shown in Table 3.1. The improved voltage for graphite channel due to the reduction of the cell resistance at 5 mA/cm² is only 6.4 ± 0.06 mV, which is much smaller than the total increased cell voltage (98±3 mV) at 5 mA/cm² compared to the PTFE channel. The

dramatic improvement in the overall performance indicates that the graphite channel may largely increase the number of active sites for the redox reaction, and also has the better mass transfer of the redox couple to the electrode surface.

Table 3.1 Cell resistances at the OCV and voltage losses at 5 mA/cm² for μ RAFCs with different channel materials.

Channel material	Cell resistance at the OCV, Ω	Voltage loss at 5 mA/cm ² , mV
Graphite channel	1.29±0.01	1.94±0.02
PTFE channel	5.53±0.04	8.30 ± 0.06



Figure 3.3 Individual electrode polarization curves for μ RAFCs with different channel materials at ambient temperature and pressure and 1 M FeSO₄/1 M H₂SO₄ at a flow rate of 0.1 ml/min.

Figure 3.3 demonstrates the individual electrode potentials for μ RAFCs with different anodes. It clearly shows that the μ RAFC with a graphite channel yields an anode performance with a much lower open circuit potential and a gentler anode potential slope than the design with a PTFE channel, indicating that the graphite channel walls enhance the reaction kinetics and local concentration of the redox couple on the electrode surface. Unlike the drop of cathode potentials after depositing extra catalyst on the channel walls in the µDMFC, the cathode performance almost remains the same for RAFCs with active walls and inactive walls. Since the oxidation of ferrous reaction cannot generate any protons, the change of the anode on the channel walls does not affect the proton transfer to the cathode, which is closely related to the measured cathode potentials. Thus, the improvement of the anode performance can totally reflect on the overall cell performance. In contrast, in the DMFC, protons are produced during the oxidation of the methanol, so the change in the anode on the walls affects the proton transfer in the system. The protons need to travel through a distance to reach the cathode, generating a depolarization on the cathode.

3.3.1.2 Thickness of the anode on the membrane

The anode catalyst loading on the membrane was adjusted by changing the number of layers of carbon paper. The total cell resistances at the OCV for RAFCs with a graphite channel combined with different layers of carbon paper are shown in Table 3.2. As discussed above, the cell resistance of the fuel cell with carbon paper layers includes the ionic resistance of the membrane, the electrical resistances of the electrodes, and current collector layers, and the contact resistances between each of the components. Therefore the cell resistances of fuel cells with one or two carbon paper layers are very similar, and the difference of 0.05 Ω is because of an extra electrical and contact resistance introduced by one more carbon paper layer. The fuel cell with no carbon paper layer has the highest cell resistance since the ionic resistance of the sulfuric

80
acidic solution is also included in the cell resistance. Figure 3.4 shows the performance of the RAFCs with a graphite channel combined with different layers of carbon paper as the anode. It is surprisingly shown that an increase in the thickness of the anode on the membrane does not improve the overall fuel cell performance. On the contrary, adding two layers of carbon paper to the RAFC decreases the cell performance by 37% compared to the case with no carbon paper in terms of maximum power density. This degradation is most likely due to the increased ionic resistance in the carbon paper layer and the cathode catalyst layer.

Number of carbon paper layer	Cell resistance at the OCV, Ω
0	3.19±0.01
1	1.37±0.01
2	1.42±0.02



Figure 3.4 The polarization and power density curves for μ RAFCs with a graphite channel and different layers of carbon paper at ambient temperature and pressure and 1 M FeSO₄/1 M H₂SO₄ at a flow rate of 0.1 ml/min.

The effect of carbon paper on the individual electrode potentials is shown in Figure 3.5. It can be seen that the thickness of the carbon paper on the membrane does not affect the anode performance, which indicates the kinetics of anode reaction was not a limiting factor to the performance in RAFCs with a graphite channel. The carbon paper on the membrane may not be completely wetted, and also the amount of water diffused to the cathode catalyst layer is reduced due to the increased thickness of the diffusion layers, leading to an increase in the ionic resistance. Therefore, cathode performance decreases with the increase of the carbon paper thickness.



Figure 3.5 Individual polarization curves for μ RAFCs with a graphite channel and different layers of carbon paper at ambient temperature and pressure and 1 M FeSO₄/1 M H₂SO₄ at a flow rate of 0.1 ml/min.

3.3.2 Operating conditions

The anolyte flow rate and sulfuric acid concentration were evaluated since they can affect the mass transfer of the redox couple, and the proton transfer.

3.3.2.1 Anolyte flow rate

The flow rate can generally affect the supply of the redox species to the electrode layer and also the redox couple crossover. The reaction rate of redox couple is much faster than the methanol-oxidation reaction, and the reaction can be limited by the exhaustion of the reactant at the electrode. Higher flow rates were evaluated for µRAFCs than for µDMFC. Figure 3.6 shows the cell polarization curves of fuel cells with a graphite channel at four flow rates of 0.1 ml/min, 1 ml/min, 2 ml/min, and 5 ml/min. A solution of 1 M FeSO₄/1 M H₂SO₄ was fed to the RAFC at ambient temperature and pressure. The results show that the overall performance improves 25% in terms of maximum power density with the increase of the flow rate from 0.1 to 2 ml/min, while the cell performance is nearly identical at the flow rates of 2 ml/min and 5 ml/min. The increase in the flow rate can accelerate the mass transfer of the redox couple and increase the concentration of the reactant on the anode surface, thus reducing the anode overpotential. The increase in flow rate can also increase the anolyte crossover to the cathode, which increases the cathode overpotential. The combination of these two effects determines the overall cell performance.



Figure 3.6 The polarization and power density curves for μ RAFCs with a graphite channel at ambient temperature and pressure and 1 M FeSO₄/1 M H₂SO₄ at different flow rates.

The effect of the anolyte flow rate on individual electrode potentials is shown in Figure 3.7. When increasing the flow rate from 0.1 ml/min to 5 ml/min, the anode performance is improved. This improvement is much more evident than in the DMFC with an increase of the anolyte flow rate. This is because the slow reaction kinetics of the anode mainly limits the performance and the mass transfer of the methanol is sufficient for most of the testing flow rates in the DMFC, while the reaction kinetics of the redox couple is fast and the mass transfer of redox species is not sufficient in the RAFC. Increasing the flow rate can enhance the anode performance by promoting the convective mass transfer of the redox couple to the active surfaces. However, increasing the flow rate also increases the redox couple crossover rate to the cathode reducing the cathode performance.



Figure 3.7 Individual electrode polarization curves for μ RAFCs with a graphite channel at different flow rates of 1 M FeSO₄/1 M H₂SO₄ solution.

3.3.2.2 Effect of sulfuric acid concentration

The reaction of the redox couple at the anode cannot produce protons, so higher acid concentrations were employed for RAFC than DMFC. Figure 3.8 shows the cell polarization curves and power density plots of RAFCs with a graphite channel at different H_2SO_4 concentrations at ambient temperature and pressure. An analyst solution of 1 M FeSO₄ mixed with different amounts of H_2SO_4 was fed to the cell at a flow rate of 0.1 ml/min. When increasing the sulfuric acid concentration from 0.5 M to 2 M, the maximum power density increases by 83%. This improvement is most likely due to the reduction of the ionic resistance. According to the EIS tests, the cell resistances at the open circuit condition are 2.89±0.01, 1.75±0.01 and 1.26±0.01 Ω at the H₂SO₄ concentrations of 0.5 M, 1 M and 2 M, respectively. This apparent enhancement for the RAFC is very different from the slight decrease in the DMFC when increasing the acid

concentration as protons are only the reactant of the cathode reaction but not the product of the anode reaction in the RAFC.

Figure 3.9 shows the effect of the H₂SO₄ concentration on individual electrode potentials. The cathode potential increases dramatically with an increase of the acid concentration. The improved cathode potentials at the open circuit condition are caused by the increase of the equilibrium potential due to the increase of the proton concentration according to equation 2.2. The enhanced proton conductivity is the other reason for the improvement of the cathode performance. As shown in Figure 3.9, the anode potentials do not change evidently with an increase of acid concentration, indicating the acid solution does not have any significant impact on the redox reaction during testing. Therefore, cathode potential increases due to the increase of the acid concentration and is reflected in the overall cell potential of the RAFC.



Figure 3.8 The polarization and power density curves for μ RAFCs with a graphite channel for different sulfuric acid concentrations/1 M FeSO₄ solution at a flow rate of 0.1 ml/min.



Figure 3.9 Individual electrode polarization curves for μ RAFCs with a graphite channel for different sulfuric acid concentrations/1 M FeSO₄ solution at a flow rate of 0.1 ml/min.

3.4 Summary

- The µRAFC with catalyzed channel walls significantly improved the anode and overall cell performances compared to the fuel cell with inactive channel walls for the redox reaction.
- The µRAFC without carbon paper layer on the membrane as the anode showed better performance compared to the µRAFCs with carbon paper. The possible reason is that the carbon paper layer inhibited the proton transport into the membrane from the electrolyte.
- When the flow rate of the anolyte was 2 ml/min and higher, the RAFC with a graphite channel achieved better performance. The increase in the flow rate could increase the local concentration of the reactant on the electrode surface of the anode, but also increase the anolyte crossover to the cathode. The combination of these two effects determines the overall fuel cell performance.
- For the RAFC with a graphite channel, the cathode potential could be increased dramatically with an increase of sulfuric acid concentration from 0.5 M to 2 M. The proton transfer was a limiting factor to the performance. Increasing the sulfuric acid concentration in the anolyte solution did not show an evident impact on the redox reaction at the anode.

Chapter 4: Modeling of micro direct methanol fuel cells with catalyzed flow field channel walls

4.1 Introduction

To have a better understanding of the interacting phenomena of electrochemical reactions and mass transport in the fuel cell design with anode catalyst on the channel walls, and the main limitations to the fuel cell performance, a three-dimensional model has been developed to predict the performance of the micro DMFC with catalyzed channel walls. The model was used to assess the effects of several important parameters (anode catalyst loading on the channel walls, ionic conductivity of the liquid-phase and solid-phase conductors, and channel geometry) on the overall cell and individual electrode performances for the two designs: i) fuel cells with anode catalyst only on the channel walls.

To develop a simplified 3D model coupling the phenomena of fluid flow, species mass transport, methanol crossover and the electrochemical reactions, the following main assumptions were made.

- 1. The fuel cell system is isothermal and at steady state.
- 2. The flow of the liquid phase in the main channel is considered to be incompressible laminar flow.
- The concentrations of the proton in the liquid acidic solution and membrane are both uniform.

- 4. The physical properties of the electrode and membrane are isotropic and homogeneous.
- 5. The methanol is completely oxidized.
- The generation of CO₂ at the anode and H₂O at the cathode is neglected, so that single phase conditions are assumed.
- 7. The reaction of methanol from crossover takes place only at the interface of the membrane and cathode catalyst layer.

The modeled fuel cell geometry for the micro air-breathing DMFC with anode catalyst both on the membrane and channel walls is shown in Figure 4.1, and the main geometrical parameters for the baseline case are listed in Table 4.1.



Figure 4.1 The modeled geometry of the fuel cell with anode catalyst deposited both on the membrane and the channel walls.

Parameter	Symbol	Value, mm
Channel length	Ι	30
Channel width	W	1
Channel height	h	1
Thickness of carbon paper (GDL)	T _{GDL}	0.25
Thickness of anode on the membrane, 0.44 mg Pt/cm ²	T _{ac, m}	0.0145
Thickness of anode on the channel walls, 0.2 mg Pt/cm ²	T _{ac, w}	0.0066
Thickness of cathode catalyst layer, 0.04 mg Pt/cm ²	T _{CC}	0.0029
Membrane thickness	T _m	0.017

 Table 4.1 Geometrical parameters for the 3D model.

4.2 Model equations

The 3D model couples the phenomena of proton and electron transport, electrochemical reactions, fluid flow, and species mass transport in the micro DMFC. The modeled phenomena and the potential boundary conditions (in 4.2.5) for the micro-DMFC with anode catalyst deposited both on the membrane and the channel walls are illustrated in Figure 4.2. It can be seen that the two anodes (wall anode and membrane anode) are electrically connected through a carbon paper. The total current (I_{total}) of the fuel cell is the sum of the current generated from the wall anode (I_{wall}) and the current from the membrane anode ($I_{membrane}$). The governing equations for these phenomena follow in the next sections.



Figure 4.2 Schematic illustration of the modeled phenomena and the potential boundary conditions in the micro-DMFC with anode catalyst deposited both on the membrane and the channel walls.

4.2.1 Proton and electron conservation equations

In fuel cells with anode catalyst on the channel walls, the functions of the liquid-phase sulfuric acid solution and the solid-phase ionomer membrane are both to transport protons generated from the anode catalyst layers. Since it has been assumed that the concentrations of the proton in the acidic solution and membrane are both uniform, the proton diffusion and the convection can be negligible. The proton transfer from the anode to the cathode is driven by electrical migration only. In this case, Ohm's law was used for solving the ionic current density i_l in the electrolyte.

$$i_l = -\sigma_{l,eff} \nabla \phi_l \tag{4.1}$$

where $\sigma_{l,eff}$ is the effective ionic conductivity of the porous media, and ϕ_l is the local electrolyte potential.

The effective ionic conductivity of the porous media with only one type of electrolyte (cathode catalyst layer, and carbon paper layer on the anode side) was defined by the Bruggeman correlation¹²:

$$\sigma_{l,eff} = \sigma_l \varepsilon_l^{1.5} \tag{4.2}$$

where σ_l is the conductivity of the electrolyte, and ε_l is the volume fraction of electrolyte in the porous media.

For the anode catalyst layer, we derived the expression for the effective electrolyte conductivity based on the assumption that the pores in the anode catalyst layers are fully saturated with the acidic electrolyte solution, and the protons travel the same distance over the same surface area through the liquid and solid conductors. The equation is given by:

$$\sigma_{l,eff} = \frac{2\sigma_{l,mem}\varepsilon_{CL,ion}^{1.5}\sigma_{l,acid}\varepsilon_{CL}^{1.5}}{\sigma_{l,mem}\varepsilon_{CL,ion}^{1.5} + \sigma_{l,acid}\varepsilon_{CL}^{1.5}}$$
(4.3)

where $\sigma_{l,mem}$ and $\sigma_{l,acid}$ are the conductivities of the ionomer and acidic solution, respectively; $\varepsilon_{CL,ion}$ and ε_{CL} are the volume fraction of the ionomer, and the porosity of the catalyst layer, respectively.

Similarly, the electrical current density i_s in the catalyst layers or carbon paper layers was also solved by Ohm's law:

$$i_s = -\sigma_s \nabla \phi_s \tag{4.4}$$

where σ_s represents the conductivity of electrical conductors; φ_s is the local electrical conductor potential.

The proton balance in the membrane and acidic solution was expressed by Equation 4.5, and Equation 4.6 shows the electron conservation in the carbon paper layer.

$$\nabla \cdot \left(\sigma_{l,eff} \nabla \phi_l\right) = 0 \tag{4.5}$$

$$\nabla \cdot (\sigma_s \nabla \phi_s) = 0 \tag{4.6}$$

In the anode catalyst layers, the charge balances are shown in equations 4.7 and 4.8.

$$\nabla \cdot \left(\sigma_{l,eff} \nabla \phi_l\right) = j_a \tag{4.7}$$

$$\nabla \cdot (\sigma_s \nabla \phi_s) = -j_a \tag{4.8}$$

In the cathode catalyst layer, the charge balances are shown by equations 4.9 and 4.10.

$$\nabla \cdot \left(\sigma_{l,eff} \nabla \phi_l\right) = -j_c \tag{4.9}$$

$$\nabla \cdot (\sigma_s \nabla \phi_s) = j_c \tag{4.10}$$

4.2.2 Electrochemical reaction models

The oxidation reaction of methanol at the anode catalyst layer is

$$CH_3OH + H_2O \to CO_2 + 6H^+ + 6e^-, \ E_a^\circ = -0.016 V.$$
 (4.11)

The modified Tafel equation was applied to determine the oxidation reaction rate⁹⁹,

$$j_a = a i_{0,a,ref} \left(\frac{C_m}{C_{m,ref}} \right)^{\beta} \left[\exp\left(\frac{\alpha_a F}{RT} \eta_a \right) \right]$$
(4.12)

where j_a is the volumetric current density at the anode, $i_{0,a,ref}$ the reference exchange current density of the anode reaction, a the active specific surface area, C_m the local methanol concentration, $C_{m, ref}$ the reference fuel concentration, α_a the charge transfer coefficient, and η_a the activation overpotential of the anode reaction ($\eta_a = \varphi_s - \varphi_l - E_{e,a}$). β is the reaction order, where $\beta = 0$ for $C_m \ge C_{m,ref}$ and $\beta = 0.5$ for $C_m < C_{m,ref}^{100}$.

The oxygen reduction reaction at the cathode catalyst layer is given by

$$\frac{3}{2}O_2 + 6e^- + 6H^+ \to 3H_2O, \qquad E_c^\circ = 1.229 \, V. \tag{4.13}$$

The reaction rate for the cathode was determined by a first-order Tafel equation⁹⁹:

$$j_{c} + j_{p} = ai_{0,c,ref} \left(\frac{C_{0}}{C_{0,ref}}\right) exp\left(-\frac{\alpha_{c}F}{RT}\eta_{c}\right)$$

$$(4.14)$$

where j_c is the volumetric current density at the cathode, j_p the parasitic volumetric current density at the cathode due to the methanol crossover, $i_{0,c,ref}$ the reference exchange current density of the cathode reaction, C_o the local oxygen concentration, $C_{o,ref}$ the reference oxygen concentration, α_c the charge transfer coefficient, and η_c the activation overpotential of the cathode reaction ($\eta_c = \varphi_s - \varphi_l - E_{e,c}$).

Equation 4.15 has been applied to determine the parasitic current density $i_p (j_p = i_p / \tau_{cc})$ in many modeling studies^{101–107}:

$$i_p = 6FN_{mCL} \tag{4.15}$$

where N_{mCL} is the average flux of methanol reaching the interface between the membrane and cathode catalyst layer.

It is often assumed that methanol reaching the cathode can be completely consumed instantly and the methanol concentration is zero at the interface of the membrane and cathode catalyst layer. However, Eccarius¹⁰⁸ concluded that methanol crossing over from the anode is not completely consumed as a significant amount of methanol was detected in the cathode outlet stream. The overpotential due to the crossover is also affected by the cathode catalyst loading. Gogel¹⁰⁹ reported the parasitic current density increased by a factor of two at the OCV with an increase of the cathode Pt loading from 1 mg/cm² to 2 mg/cm². In our study, methanol on the cathode side is not likely to be completely oxidized due to the very low cathode catalyst loading (Pt 0.04 mg/cm²). A correction term γ was added to equation 4.15 to take into account the discrepancy between the reality and assumption. γ is a parameter related to the methanol reaction rate at the cathode and its value was fitted according to the experimental data.

$$i_p = 6FN_{mCL}\gamma \tag{4.16}$$

4.2.3 Fluid flow models

Neglecting body forces, the incompressible laminar flow in the micro-channel was described by the continuity and Navier-Stokes equations:

$$\nabla \cdot \vec{u} = 0 \tag{4.17}$$

$$\rho(\vec{u} \cdot \nabla \vec{u}) = -\nabla P + \mu \nabla^2 \vec{u} \tag{4.18}$$

where \vec{u} is the velocity vector of the fluid, ρ is the liquid density, P is the static pressure, and μ is the dynamic viscosity. In porous media, such as diffusion layers, membrane, and electrode layers, the pressure distribution was solved based on the Brinkman equation¹¹⁰.

$$\frac{\rho(\vec{u}\cdot\nabla\vec{u})}{\varepsilon^2} = -\nabla P - \frac{\mu}{K}\vec{u} + \frac{\mu}{\varepsilon}\nabla^2\vec{u}$$
(4.19)

where K and ε are the permeability and porosity of the porous media, respectively.

4.2.4 Mass transport models

The mass conservation equation for the fuel was given by:

$$\nabla \cdot (-D_m \nabla C) + \vec{u} \nabla \cdot C_m = S_m \tag{4.20}$$

where D_m is the diffusion coefficient for methanol, C_m is the local concentration of methanol and the source term S_m is the net rate of methanol consumption. At the anode catalyst layers, S_m is given by

$$S_m = -\frac{J_a}{6F}.$$
(4.21)

The methanol flux through the membrane N_m was written as:

$$N_m = \nabla \cdot (-D_m \nabla C) + \vec{u} \cdot \nabla C_m - n_d^{MeOH} \frac{i}{F}$$
(4.22)

$$n_d^{MeOH} = n_d^{Water} x_{MeOH} \tag{4.23}$$

97

The three terms on the right side of equation 4.22 represent the methanol crossover caused by diffusion, convection, and electro-osmotic drag, respectively. n_d^{MeOH} and n_d^{Water} are the electro-osmotic drag coefficient of methanol and water, respectively. x_{MeOH} is the mole fraction of methanol.

For the air-breathing cathode, the behavior of oxygen diffusion through porous carbon paper and catalyst layers was governed by the Maxwell-Stefan diffusion model¹¹¹. Neglecting the influence of water vapor, the equation can be written as

$$\nabla \left\{ -\rho_g \omega \sum_{j=1}^2 D_{O,eff} \left[\frac{M}{M_j} \left(\nabla \omega_j + \omega_j \frac{\nabla M}{M} \right) + \left(x_j - \omega_j \right) \frac{\nabla P}{P} \right] \right\} = S_o$$
(4.24)

where ρ_g is the density of the gas mixture, ω the mass fraction, $D_{O,eff}$ the diffusion coefficient of oxygen, *M* the molecular mass, x_j the molar fraction and S_O the reaction term accounting for the consumption of oxygen in the cathode catalyst layer.

$$S_o = -\frac{J_c + J_p}{4F} \tag{4.25}$$

The effective diffusion coefficient in the porous media was calculated by the Bruggeman correction equation:

$$D_{o,eff} = D_o \varepsilon^{1.5} \tag{4.26}$$

where D_o is the diffusion coefficient of oxygen in air.

4.2.5 Boundary conditions

Boundary conditions are necessary to solve all the governing equations.

For the equations of proton and electron transfer, the boundary conditions were defined as shown in Figure 4.2.

$$\varphi_s = E_{ground}$$
 at the end of the anode electrical conductor (4.27)

 $\varphi_s = E_{cell}$ at the interface of the cathode carbon paper and the air (4.28)

where E_{ground} is a fixed electric potential (0 V) used to ground the voltage at an external boundary, and E_{cell} is the applied cell voltage.

For the domains of methanol transfer, the boundary conditions at the inlet of the channel under baseline case were set to 1.67×10^{-9} m³/s (0.1 ml/min) for the volumetric flow rate and 1000 mol/m³ for the methanol concentration, which are similar to the experimental conditions. At the interface of the cathode catalyst layer and the membrane, the methanol concentration was zero. At the outlet of the fuel channel, the boundary condition shown in equation 4.29 and ambient pressure were applied. No-flux boundary was set to all the other boundaries. No slip boundary condition was used to all the walls of the fuel flow domains.

$$-\boldsymbol{n} \cdot \boldsymbol{D}_m \nabla \mathbf{C} = 0 \tag{4.29}$$

For the oxygen transfer, the boundary conditions were set to ambient pressure and 23.3 wt.% oxygen in the air at the interface of air and the GDL. No-flux and no slip boundary conditions were set for all the other walls of air flow domains.

All the governing equations of proton and electron transfer, electrochemical reactions, fluid flow, and species mass transfer were implemented by the commercial software

COMSOL Multiphysics 5.2 using the stationary segregated Parallel Direct Sparse Solver (PARDISO). The linear method was used for the discretization. Convergence of the numerical solution was guaranteed by setting the relative tolerance to a criterion of less than 10⁻³ for the continuity, momentum, mass transport, and proton and electron transport variables.

4.3 Comparison with experimental data

The model was developed based on the fitting of the experimental data shown in Figure 2.4 and Figure 2.5 of Chapter 2. The main parameters under the baseline operating conditions are listed in Table 4.2.

Table 4.2 Parameters used in the model.

Parameter	Symbol	Value	Unit	Source
Temperature	Т	293.15	K	**
Inlet methanol concentration	C _m	1000	mol/m ³	**
Inlet flow rate	Q _m	1.67×10 ⁻⁹	m³/s	**
Anode fluid density	ρ	998	Kg/m ³	**
Fluid dynamic viscosity	μ	1×10 ⁻³	Pa∙s	**
Air density	$ ho_g$	1.2	Kg/m ³	**
Air viscosity	μ_g	1.82×10 ⁻⁵	Pa∙s	**
Oxygen mass fraction in the air	ω_o	0.233		**
Electric conductivity of cathode GDL	$\sigma_{\text{s, GDLc}}$	255	S/m	**
Electric conductivity of anode GDL	$\sigma_{\text{s, GDLa}}$	1250	S/m	**
Electric conductivity of catalyst layer	$\sigma_{\rm s,\ CL}$	164	S/m	**
Proton conductivity of membrane	$\sigma_{l, mem}$	0.52	S/m	**
Proton conductivity of acidic solution	$\sigma_{l, acid}$	3.7	S/m	**
(0.1 M H ₂ SO ₄ /1 M methanol)				
Exchange current density of the wall anode	İ _{0, aw, ref}	0.012	A/m ²	*

Parameter	Symbol	Value	Unit	Source
Exchange current density of the membrane	la a ref	0.048	A/m ²	*
anode	10, a, iei	0.010	/ / / / /	
Exchange current density of the cathode	i _{0, c, ref}	0.00055	A/m ²	*
Active specific surface area	а	1×10 ⁴	1/m	*
Equilibrium anode potential	E _{e, a}	0.016	V	**
Equilibrium cathode potential	E _{e, c}	1.219	V	**
Reference methanol concentration	C _{m, ref}	1000	mol/m ³	*
Reference oxygen concentration	Co, ref	0.52	mol/m ³	*
Transfer coefficient of the anode	α _a	0.5		*
Transfer coefficient of the cathode	α_c	0.58		*
Porosity of GDL	ε _{GDL}	0.7		112
Porosity of catalyst layer	ε _{CL}	0.4		*
Porosity of membrane	E mem	0.28		113
lonomer volume fraction within catalyst	S ource	03		112
layers	CL, ion	0.0		
Diffusion coefficient of methanol in anode	Dm cla	1x10 ⁻¹¹	m²/s	*
catalyst layer	Dill, CLa		11170	
Diffusion coefficient of methanol in	D	1 8×10 ⁻¹⁰	m²/s	103
membrane	₽m, mem	1.0×10	11175	
Diffusion coefficient of oxygen in air	Do	2.05×10⁻⁵	m²/s	113
Permeability of cathode GDL	K _{GDLc}	1.92×10 ⁻¹⁴	m²	**
Permeability of anode GDL	K _{GDLa}	1.22×10 ⁻¹¹	m²	114
Permeability of catalyst layers	K _{CL}	1.5×10 ⁻¹⁴	m ²	112
Permeability of membrane	K _{mem}	1.8×10 ⁻¹⁸	m²	115
Electro-osmotic drag coefficient of water	n_d^{Water}	2.5		107
Correction factor for parasitic current	Y	0.16		*

*These values were assumed based on the comparison of the simulation results with the experimental data. **These parameters were determined according to the experimental materials and

conditions.

To get fuel cell polarization curves, the equations were solved at different fuel cell voltages. The geometrical surface area of the membrane was employed to calculate the current densities. For the baseline case, the geometrical area of the membrane is 0.3 cm^2 (length×width=3 cm×0.1 cm=0.3 cm²).

During the experimental study, the reference electrode was placed in the outlet solution. To be consistent with the experiment, the anode potential E_a and cathode potential E_c in the model were defined as:

$$E_a = E_{ground} - \varphi_{l,outlet} \tag{4.30}$$

$$E_c = E_{cell} - \varphi_{l,outlet} \tag{4.31}$$

where $\varphi_{l, outlet}$ is the average electrolyte potential φ_l at the fluid channel outlet as shown in Figure 4.1.

Figure 4.3 and Figure 4.4 show the comparison of the modeling results with experimental data in terms of the fuel cell and individual electrode polarization plots for micro DMFCs with different anode catalyst distributions. The baseline case conditions were applied to all the designs, 1 M methanol/0.1 M sulfuric acid solution at an inlet flow rate of 0.1 ml/min.



Figure 4.3 Comparison of modeling and experimental polarization curves for µDMFCs with different anode catalyst distributions at ambient temperature and pressure and 1 M methanol/0.1 M sulfuric acid at a flow rate of 0.1 ml/min.



Figure 4.4 Comparison of modeling and experimental individual electrode polarization plots for the µDMFCs of Figure 4.3 with different anode catalyst distributions.

The trend of the predicted fuel cell performance for the three fuel cell designs is the same as that for the experimental data. The fuel cell with anode catalyst deposited both on the channel walls and the membrane gains the highest cell performance, while the fuel cell with anode catalyst only on the walls has the lowest performance.

The predicted voltages in the higher current density region are very close to the experimental value except for the fuel cell with anode catalyst only on the walls. The largest deviations between the predicted values and the experimental values are in the region of the open circuit conditions. According to the individual electrode potentials shown in Figure 4.4, the disagreement at the open circuit condition is mainly due to the anode side. A mixed potential could be generated by the reaction of some impurity at the anode during the experimental measurements. The model also overestimated the cathode performance of the fuel cell with catalyst only on the channel walls. This disagreement could be due to neglecting some of the significant impacts of the methanol crossover. As with the majority of the DMFC models in the literatures^{116–119}, our present model only includes the influence of the parasitic current caused by the reaction of methanol crossover from the anode to the cathode on the cathode performance, but this may underestimate the effect of the methanol crossover. Methanol crossover could reduce the cathode performance mainly in three aspects¹²⁰: 1) generating a mixed potential through the methanol oxidation, 2) poisoning the active sites of the cathode Pt catalyst, and 3) reducing the oxygen concentration on the cathode active catalyst sites. Tamaki et al.¹²¹ reported the CO poisoning of the Pt catalyst increased the cathode overpotential sharply after the flux of methanol crossover

reached a certain threshold value, and a lower Pt loading on the cathode results in a lower threshold methanol crossover value. The Pt poisoning could have a crucial effect on the cathode performance especially when the cathode Pt loading is low. Also, Kulilovsky¹²² developed a model for the mixed potential considering the effect of methanol crossover and poor oxygen transport in the electrode, and reported the methanol crossover reduced the local oxygen concentration in the cathode catalyst layer and brought about an increase in the local potential loss.

The methanol fluxes obtained through our model at the interface of cathode catalyst and membrane as a function of current density for the three designs are shown in Figure 4.5. The average methanol flux is much higher for the fuel cell with anode catalyst only on the channel walls compared to the other designs with an anode catalyst layer on the membrane. Also, the cathode catalyst loading is relatively low (0.04 mg/cm² Pt) in the tested fuel cells, thereby the poisoning of the cathode catalyst and the reduction of the oxygen concentration could play an important role in raising the cathode overpotential during the experimental measurements, especially in fuel cells without an anode catalyst layer on the membrane. However, to the best of our knowledge, mechanistic model considering the combined effects of Pt poisoning and competition of oxygen and methanol on the Pt surface is unavailable.



Figure 4.5 Methanol crossover fluxes at the interface of the membrane and cathode for fuel cell designs with different anode catalyst distributions.

4.4 Model application for evaluating important parameters

The performance of the DMFC is mainly determined by the utilization and active surface area of the catalyst, ohmic resistance, and mass transfer of methanol and oxygen. In fuel cell designs with anode catalyst on the walls, the anode catalyst loading and distribution could significantly affect the utilization and active surface area of the catalyst, proton transfer, and methanol transfer; the ionic conductivities of acidic solution and solid ionomer have a crucial influence on ohmic losses; the channel geometry could affect both the ohmic losses and mass transfer of methanol. The effects of these parameters on the fuel cell performance were studied by the developed model.

4.4.1 Effect of anode catalyst loading on the channel walls

Figure 4.6 and Figure 4.7 show the modeled effect of the catalyst loading on the channel walls on the fuel cell and individual electrode performance for micro DMFCs with anode catalyst deposited both on the membrane and channel walls.



Figure 4.6 Modeling results of the effect of anode catalyst loading on the channel walls on the performance of the μ DMFCs with anode catalyst deposited both on the channel walls and membrane at ambient temperature and pressure and 1 M methanol/0.1 M sulfuric acid at a flow rate of 0.1 ml/min. CCM anode loading constant at 0.44 mg/cm².

It can be seen from Figure 4.7 that the increased catalyst loading on the walls enhances the anode performance as expected, but the cathode performance decreases at the same time. This trend of anode and cathode performance changes with the anode catalyst loading on the walls was also observed during the experimental testings. The increased anode performance with anode catalyst loading reflects the improvement in overall performance as shown in Figure 4.6, but this improvement in overall performance was not observed during the experiment. The decrease of the cathode performance in the modeling results is not as much as that observed in the experimental testing.



Figure 4.7 Modeling results of individual electrode performance for the µDMFCs of Figure 4.6 with anode catalyst deposited both on the membrane and channel walls.

From the simulation results, the drop of the cathode performance with the increase of the anode catalyst loading is mainly due to the ionic ohmic loss. Figure 4.8 shows the total ohmic potential losses for proton transfer through the acid solution in the flow channel and the GDL layer. The ionic potential losses on the walls increase much faster with the increase of the current density in the fuel cell with a higher anode catalyst loading than the lower catalyst loading. This is due to the increase in the proportion of current generated from the catalyzed walls with an increase of the anode catalyst loading on walls as shown in Figure 4.9. When operating at the same total current

density, the fuel cell with more catalyst on the walls produces more current and protons at the walls reducc1cing the total activation losses of the anode. But the protons generated on the walls have to transport through a longer distance to reach the cathode than the proton generated from the CCM, leading to an increase in the ohmic loss, and therefore a decrease in the cathode performance.



Figure 4.8 lonic potential losses in the acidic solution for different anode catalyst loadings on the channel walls for μ DMFCs with anode catalyst deposited both on the membrane and channel walls.



Figure 4.9 Current density generated from the catalyzed wall for different anode catalyst loadings on the channel walls of μ DMFCs with anode catalyst deposited both on the membrane and channel. i_{wall} is based on the geometrical area of the channel walls (0.9 cm²).

The methanol crossover only slightly increases with an increase of the anode catalyst loading on the wall according to our modeling results of the average methanol flux at the interface of the cathode catalyst layer and membrane as shown in Figure 4.10. The influence of the change in methanol crossover on the performance is not as significant as the impact of the ionic ohmic losses. In order to improve the performance of fuel cells with anode catalyst both on the membrane and channel walls through increasing the loading on the walls, it is important to reduce the resistance of the ionic electrolyte conductor so that the improvement due to the extra catalyst will not be counteracted by the ohmic losses.



Figure 4.10 Methanol crossover flux at the interface of the membrane and cathode for different anode catalyst loadings on the channel walls of μ DMFCs with anode catalyst deposited both on the membrane and channel walls.

Figure 4.11 and Figure 4.12 show the effect of the catalyst loading only on the channel walls on the fuel cell and individual electrode performances of micro DMFCs with anode catalyst deposited only on the channel walls. The performance improvement due to the increase of the catalyst loading is much more obvious than the fuel cell with anode catalyst both on the membrane and walls. It can be seen from Figure 4.12 that the higher loading on the walls clearly enhances the anode performance, indicating the kinetics of the anode reaction is a major limitation to the anode performance. Different from the fuel cell with both the wall anode and the membrane anode, the proportion of current generated from the catalyzed walls is not affected by the anode catalyst loading on the channel walls. Therefore the ionic resistance and the cathode performance are not affected by the anode catalyst loading on the channel walls.



Figure 4.11 Modeling results of the effect of anode catalyst loading on the channel walls on the performance of μ DMFCs with anode catalyst deposited only on the channel walls at ambient temperature and pressure and 1 M methanol/0.1 M sulfuric acid at a flow rate of 0.1 ml/min.



Figure 4.12 Modeling results of the effect of anode catalyst loading on the channel walls on the individual electrode performance for μ DMFCs of Figure 4.11 with anode catalyst deposited only on the channel walls.

4.4.2 Effect of anode catalyst distribution

In our study, adding extra anode catalyst loading on the channel walls exhibited improved cell performance for the bipolar designed fuel cell. However, increasing the anode catalyst loading on the membrane can also improve the cell performance under certain conditions. It could be helpful to compare the performance of fuel cells with or without catalyzed channel walls when they have the same total anode catalyst amount. The model was applied to compare the performances of the fuel cells with the same total anode catalyst amount as shown in Table 4.3. The fuel cell with a CCM and a wall anode has the same anode catalyst loading on each side of the channel wall and on the membrane, and the conventional fuel cell with just a CCM has all the anode catalyst on the membrane.

Anode	Membrane anode,	Wall anode,	Total anode
distribution	0.3 cm ²	0.9 cm ²	catalyst amount
CCM only	0.44 mg/cm² (14.5 μm)	0	0.132 mg
CCM & Wall	0.11mg/cm ² (3.625 µm)	0.11mg/cm ² (3.625 μm)	0.132 mg

Table 4.3 Anode catalyst loadings for fuel cells with different anode catalyst distributions.

It can be seen from Figure 4.13 and Figure 4.14 that the typical fuel cell with just a CCM exhibits better individual electrode and overall cell performances. In our model, the exchange current density of the reaction at the anode on the membrane is higher than that of the anode reaction on the channel walls based on the fitting of the experimental data; which means the anode reaction on the membrane has a faster reaction rate. Distributing the anode catalyst from the membrane to the channel walls mainly improves the mass transfer of methanol, and the fuel cell with catalyzed channel wall exhibits a higher average methanol concentration at the anode catalyst layer as shown in Figure

4.15. The limiting factor for the anode performance is the reaction rate at the catalyst surface and not the mass transfer. Therefore, adding the same amount of anode catalyst on the membrane exhibits a better anode performance than adding the catalyst on the walls.

Although the performance of the fuel cell with catalyzed channel walls is not as good as the typical fuel cell with a CCM only when using the same total anode catalyst amount of 0.132 mg, increasing the loading on the membrane cannot always improve the performance due to the mass transfer limitation. When the anode catalyst loading on the membrane reaches its optimum value and the mass transfer becomes a dominant factor, adding more anode catalyst on the membrane cannot improve the performance, but depositing the extra anode catalyst on the channel walls still can improve the cell performance due to its good methanol transfer.



Figure 4.13 Modeling results of the effect of anode catalyst distribution on the performance of μ DMFCs with the same total anode catalyst amount at ambient temperature and pressure and 1 M methanol/0.1 M sulfuric acid at a flow rate of 0.1 ml/min.



Figure 4.14 Modeling results of the effect of anode catalyst distribution on the individual electrode performance for µDMFCs of Figure 4.13 with the same total anode catalyst amount.



Figure 4.15 The modeled effect of the anode catalyst distribution on the average methanol concentration at the anode catalyst layer of µDMFCs with the same total anode catalyst amount.

4.4.3 Effect of ionic conductivity of liquid phase

The performance of fuel cells with anode catalyst on the channel walls can be affected significantly by the ionic conductivity, and therefore the model was applied to study the effect of ionic conductivities of the liquid-phase acidic solution and solid-phase ionomer.

Figure 4.16 and Figure 4.17 show the effect of the ionic conductivity of the liquid acidic solution on the cell and individual electrode performance of micro DMFCs with anode catalyst deposited both on the membrane and the channel walls. The values of 3.7, 25.1, and 44.2 S/m are corresponding to the conductivities of solutions containing 1 M methanol mixed with 0.1 M, 0.5 M, and 1 M sulfuric acid⁸¹, respectively. All the other design and operating parameters are under the baseline case. The increase of the solution ionic conductivity from 3.7 S/m to 25.1 S/m reduces the transfer resistance of the proton generating on the channel walls, leading to an improvement in the cathode, but also a slight drop for anode performance. This trend is the same as the experimental result. However, the slight improvement in the simulated overall performance was not observed during the experiment. The decrease of the anode performance in the modeling results is not as much as that in the experiment. This may due to the neglect of the effect of loss of Pt performance caused by the bisulfate anion.


Figure 4.16 The modeled effect of the acidic solution conductivity on the performance of μ DMFCs with anode catalyst deposited both on the membrane and channel walls at ambient temperature and pressure and 1 M methanol at a flow rate of 0.1 ml/min.



Figure 4.17 The modeled effect of the acidic solution conductivity on the individual electrode performance for the μ DMFCs of Figure 4.16 with different concentrations of sulfuric acid.

According to the current density generated on the catalyzed channel walls as shown in Figure 4.18, the increase of the sulfuric acid concentration from 0.1 M to 0.5 M improves the contribution proportion of the anode on the walls to the overall anode performance, reducing the improvement in cathode performance due to the decreased ionic resistance and leading to a slight performance drop for the anode performance due to the lower activity of anode catalyst on the channel walls. For the sulfuric acid solution of 0.5 M and higher, the contribution of the anode on the channel walls has no obvious change, the fuel cell performance also does not show any improvement. When the sulfuric acid concentration is 0.5 M and higher, the solution conductivity is not a limiting factor to the performance under the testing conditions.



Figure 4.18 Modeling results of the current density generated from the catalyzed wall for different conductivities of acidic solutions for the μ DMFCs of Figure 4.16. i_{wall} is based on the geometrical area of the channel walls (0.9 cm²).



Figure 4.19 Modeling results of the effect of the acidic solution conductivity on the performance for the μ DMFCs with anode catalyst deposited only on the channel walls at ambient temperature and pressure and 1 M methanol at a flow rate of 0.1 ml/min.



Figure 4.20 Modeling results of the effect of the acidic solution conductivity on the individual electrode performance for the μ DMFCs of Figure 4.19.

Figure 4.19 and Figure 4.20 show the effect of the ionic conductivity of the acidic solution on the fuel cell and the individual electrode performance of the fuel cell with anode catalyst only on the channel walls. The results have a similar trend as fuel cells with anode catalyst both on the membrane and channel walls. Since all the anode current is generated from the anode on the channel walls, the improved ionic conductivity can benefit all the anode current. The improvement of the fuel cell performance with an increase of the solution ionic conductivity is more obvious than that in Figure 4.16 and Figure 4.17, in which the solution conductivity only affects the anode performance when the sulfuric acid concentration is 0.5 M and higher.

4.4.4 Effect of ionic conductivity of solid phase conductor

Figure 4.21 and Figure 4.22 demonstrate the effect of the ionic conductivity of the solidphase conductor on the cell and individual electrode performance for micro DMFCs with anode catalyst deposited both on the membrane and channel walls. The solid phase ionic conductor includes the proton exchange membrane and the ionomer in the catalyst layers. The measured ionic conductivity for the Gore membrane in 0.1 M sulfuric acid is 0.52 S/m (See Appendix D). The values of 3.53 S/m and 9.6 S/m were chosen to study the effect of enhancement in ionic conductivity of the membrane. The solid-phase ionic conductivity is increased by the same multiple (from 0.52 S/m to 3.53 S/m) as the increase of liquid-phase conductivity (from 3.7 S/m to 25.1 S/m). The conductivity value for a Gore® membrane (9.6 S/m) results in excellent performance¹²³.



Figure 4.21 Modeling results of the effect of the solid-phase ionic conductivity on the performance of μ DMFCs with anode catalyst deposited both on the membrane and channel walls at ambient temperature and pressure and 1 M methanol/0.1 M sulfuric acid at a flow rate of 0.1 ml/min.



Figure 4.22 Modeling results of the effect of the solid-phase ionic conductivity on the individual electrode performance for the μ DMFCs of Figure 4.21.

As expected the increase of the ionic conductivity from 0.52 S/m to 3.53 S/m reduces the ohmic loss and thereby improves the cathode and overall cell performance. The performance improvement in Figure 4.21 is more obvious than that in Figure 4.16 when the ionic conductivity was increased by the same multiple. Different from the acidic solution, the solid phase ionic conductivity does not significantly change the contribution proportion of current generated on the walls as shown in Figure 4.23. The conductivity of acidic solution mainly affects the transport of protons generated through the anode catalyst on the walls, while the solid-phase ionic conductor in the catalyst layer and the membrane affect the transfer of all the generated protons. For the fuel cell with anode catalyst both on the membrane and channel walls, the conductivity is 3.53 S/m and higher, the fuel cell performance has no obvious change, indicating the solid ionic conductivity is not a limitation to the fuel cell performance.



Figure 4.23 Modeling results of the current density generated from the catalyzed wall with different conductivities of the solid-phase ionic conductor for the μ DMFCs of Figure 4.21. i_{wall} is based on the geometrical area of the channel walls (0.9 cm²).



Figure 4.24 Modeling results of the effect of the solid-phase ionic conductivity on performance for μ DMFCs with anode catalyst deposited only on the channel walls at ambient temperature and pressure and 1 M methanol/0.1 M sulfuric acid at a flow rate of 0.1 ml/min.



Figure 4.25 Modeling results of the effect of the solid-phase ionic conductivity on the individual electrode performance for the µDMFCs of Figure 4.24.

Figure 4.24 and Figure 4.25 show the effect of the solid phase ionic conductivity on the cell performance and the individual electrode performance for micro DMFCs with anode catalyst only on the channel walls. The increase of the ionic conductivity from 0.52 S/m to 3.53 S/m results in only a slight improvement in the cathode and overall cell performance due to the reduction of the ionic resistance in the catalyst layers and membrane. The conductivity of the solid phase does not affect the performance of the fuel cells with anode catalyst only on the walls as significantly as the conductivity of the solution since the proton travels a much longer distance through the liquid phase, i.e., higher charge resistance.

4.4.5 Effect of channel geometry

In the experiment, a fuel cell with the channel dimensions of $1 \text{ mm} \times 1 \text{ mm} \times 30 \text{ mm}$ was investigated. The model simulated the fuel cell performance with dimensions similar to those of the experiments, as well as much smaller dimensions of 0.1 mm \times 0.1 mm \times 30 mm and much larger dimensions of 10 mm \times 10 mm \times 30 mm to study the effect of channel dimensions on the performance of the fuel cell with anode catalyst on the walls. The smaller dimensions with catalyst on the channel walls would be difficult to achieve experimentally. The anode catalyst loading of 0.2 mg/cm² Pt on the walls was used for all the modelings. Experimentally, the deposition of anode catalyst on the walls of a smaller channel through a spraying method would be difficult because the catalyst on the walls occupies the volume in the channel, especially for a higher catalyst loading.



Figure 4.26 Modeling results of the effect of the channel dimensions on the performance of μ DMFCs with anode catalyst deposited both on the membrane and channel walls under 1 M methanol/0.1 M sulfuric acid solution at a flow rate of 0.1 ml/min.



Figure 4.27 Modeling results of the effect of the channel dimensions on the individual electrode performance for the μ DMFCs of Figure 4.26.

Figure 4.26 and Figure 4.27 show the comparison of the fuel cell performance and the individual electrode performances of the micro DMFCs for three different channel dimensions. The μ DMFCs have anode catalyst both on the membrane and channel walls. The current densities were all calculated based on the geometrical area of the membrane, which is 0.03 cm², 0.3 cm², or 3 cm² for different channel dimensions from the smallest to the largest, respectively. The results indicate that the fuel cell with a smaller channel has better anode performance, and better cathode and overall cell performance in the higher current density region. The slight improvement in the anode catalyst layer on the membrane as shown in Figure 4.28. At the same inlet flow rate, the increased flow velocity with the reduction of the channel dimension improves the

methanol transfer mainly in the channel and the carbon paper layer, which lowers the methanol concentration gradient near the anode catalyst layer, thereby enhancing the reaction rate.

For the fuel cell with a smaller channel, the slight improvement of the cathode potential at the higher current density is due to the lower resistance of proton transfer through the liquid-phase, while the decreased cathode potential at the OCV is caused by the increased average methanol crossover flux as shown in Figure 4.29 at the interface of the membrane and the cathode layer. If the issue of methanol crossover could be limited to a certain degree in the smaller channel, the reduction of the channel size would exhibit superior overall performance in terms of power density. A fuel cell with smaller channels would generally reduce the total channel volume but improve the total power of the fuel cell compared to a fuel cell with larger channels under the same geometric areas of the MEA and channel walls. The design with catalyzed channel walls would be very suitable for the applications in portable electronic devices due to the requirements of high power densities at a small footprint.



Figure 4.28 The modeled effect of the channel dimensions on the average methanol concentration at the anode catalyst layer on the membrane for the µDMFCs of Figure 4.26.



Figure 4.29 The modeled effect of the channel dimensions on the average methanol crossover flux at the interface of the membrane and cathode for the μ DMFCs of Figure 4.26.



Figure 4.30 Modeling results of the effect of the channel dimensions on the performance of μ DMFCs with anode catalyst deposited only on the channel walls under 1 M methanol/0.1 M sulfuric acid solution at a flow rate of 0.1 ml/min.



Figure 4.31 Modeling results of the effect of the channel dimensions on the individual electrode performance for the μ DMFCs of Figure 4.30.

The methanol crossover is expected to increase with a reduction of the channel size, and the methanol crossover is a dominant factor determining the fuel cell performance in the fuel cell with anode catalyst only on the channel walls due to the higher methanol flux. To examine the effect of channel dimensions on other phenomena, the model neglects the effect of methanol crossover on the cathode performance for the micro DMFCs with anode catalyst only on the channel walls. Figure 4.30 and Figure 4.31 show the effect of the channel dimensions on the cell and individual electrode performance neglecting the methanol reaction on the cathode. The results indicate reducing the channel size can improve the cathode and overall cell performance, especially in the higher current density region. The cathode performance is improved due to the decrease of ionic potential loss in the acidic solution, as shown in Figure 4.32. The decrease of the ionic potential loss in the liquid is due to the reduction of the average proton transfer distance from the anode surface to the membrane. The anode performance is not affected by the channel size, indicating methanol mass transport is not a limiting factor in the fuel cell with anode catalyst only on the walls.



Figure 4.32 The modeled effect of channel dimensions on the ohmic potential losses in the acidic solution for the µDMFCs of Figure 4.30.

4.5 Summary

• A simplified 3D model for the fuel cell designs with anode catalyst on the walls was developed. The model input parameters for catalyst loadings were based on the experimental fuel cell designs with three different anode catalyst distributions of, 1) 0.44 mg/cm² Pt catalyst only on the membrane, 2) 0.2 mg/cm² Pt catalyst only on the channel walls, 3) 0.44 mg/cm² Pt catalyst on the membrane and 0.2 mg/cm² Pt catalyst on the channel walls. The modeling results indicated good agreement with the experimental data in the higher current density region, and all the trends were similar to those of the experimental data in terms of cell potential and individual electrode potentials. The model results showed the methanol crossover flux of the fuel cell with anode catalyst only on the walls was much

higher than the other designs, resulting in poor cathode potential and cell voltage performances.

- The increase of the anode catalyst loading on the channel walls could improve the anode performance, but when there was additional anode catalyst also on the membrane, the increased contribution proportion of the anode on the walls leads to an extra ionic potential loss.
- Under the baseline case, the performance of fuel cells with anode catalyst both on the channel walls and on the membranes is more affected by the conductivity of the solid-phase ionic conductor, and the conductivity of the acidic solution could affect the contribution proportion between anode catalyst on the channel walls and anode catalyst on the membrane to the total performance. The performance of the fuel cells with anode catalyst only on the channel walls is more affected by the conductivity of the liquid solution.
- For the fuel cells with anode catalyst both on the membrane and the channel walls, the reduction of the channel dimensions could affect the anode performance by increasing the methanol concentration on the CCM, and the cathode performance by increasing methanol crossover and reducing the ionic resistance. For the fuel cells with anode catalyst only on the walls, the channel size does not affect the anode performance but affects the cathode performance by reducing the ionic resistance with reduced channel size.

Chapter 5: Conclusions and recommendations

5.1 Conclusions

The objectives of this research project were as follows:

- Development of an air-breathing micro direct methanol fuel cell (µDMFC) with catalyzed flow field channels and investigation of the effects of critical design parameters and operating conditions on its performance
- Demonstration of the application of the design of fuel cells with catalyzed flow field channel walls to the anode redox fuel cell, and determination of appropriate design parameters and operating conditions.
- Development of a 3D simplified computational µDMFC model to simulate the behaviors in the fuel cells with catalyzed channel walls and identification of important parameters determining the fuel cell performance.

In the following section, the overall conclusions regarding the objectives and the contribution of the research are discussed.

5.1.1 Micro direct methanol fuel cell with catalyzed flow field channel walls

In this work, an air-breathing micro-DMFC with extra anode catalyst deposited on the channel walls was developed. The maximum power density was 1.2 mW/cm² under conditions of ambient temperature and pressure, and 1 M methanol/0.1 M sulfuric acid at a flow rate of 0.1 ml/min. The fuel cell with extra anode catalyst (0.2 mg/cm² Pt) on the channel walls improved the maximum power density by 20% when compared to the conventional fuel cell with a CCM only (0.44 mg/cm² Pt for the anode and 0.04 mg/cm²

Pt for the cathode on the membrane). To the best of our knowledge, there is only one report in the literature that indicates that extra catalyst on the channel walls can improve the performance of the anode in an anode half cell⁸¹. Our findings further demonstrate the fuel cell with extra anode catalyst on the channel walls can improve both the anode and overall fuel cell performance when compared with the conventional design. This finding is important as the design of catalyzed channel walls has been shown to be a feasible approach to enhance the fuel cell performance by increasing the total catalyst loading without affecting the size of the micro fuel cell, and the porosity or thickness of the anode catalyst layer on the membrane.

For the design of fuel cells with anode catalyst both on the membrane and the channel walls, it was found that increasing the anode catalyst loading on the wall from 0.2 mg/cm² to 0.5 mg/cm² did not improve the cell performance. It is believed that the extra anode catalyst loading on the walls resulted in an increased overall ionic resistance, which was reflected in a drop of the cathode performance. The electrolyte proton conductivity was a limiting factor to the fuel cell performance. It is important to consider the combined effects of the reduced activation loss at the anode and the increased ohmic losses when increasing the loading on the channel walls.

The effect of methanol concentration is well known for a conventional fuel cell design in the literature. The methanol concentration generally impacts the coverage of the active sites on the anode side, and the methanol crossover to the cathode side. In this work, it was found that the fuel cell with anode catalyst both on the membrane and the channel

walls improved the performance more significantly at a low methanol concentration (0.1 M) compared with the conventional fuel cell design with a CCM only, and the current density at a cell voltage of 0.02 V was increased by 85%. It is believed that the mass transport of methanol to the catalyst active sites is more efficient in the fuel cell with anode catalyst on both the membrane and channel walls than the conventional fuel cell.

The fuel flow rate generally affects the supply of the methanol to the catalyst layer and the removal of the carbon dioxide for a conventional fuel cell design as reported in the literature. In our work, it was found the current density at low cell voltage (0.02 V) was larger for the fuel cell with extra catalyst on the channel walls compared with the conventional fuel cell with a CCM only when operated at very low fuel flow rate (0.001 ml/min). The methanol has better access to the catalyst active sites on the channel walls than to the catalyst layer on the membrane in the conventional bipolar design. Different from the conventional design, the individual cathode performance declined due to the insufficient removal of the CO₂ in both the diffusion layer and the channel at a very low fuel flow rate for the fuel cells with catalyzed walls. It is believed that the unremoved CO₂ in the system inhibits the transfer of the protons generated by the anode on the channel walls, leading to a rise in the cathode overpotential.

The addition of sulfuric acid to the methanol solution as a supporting electrolyte can enhance the proton conductivity in the conventional fuel cell⁸⁶ but decrease the anode active sites due to blockage from the bisulfate anion. In our study, for the fuel cell with extra catalyst on the channel walls, it was found that adding 0.01-0.1 M sulfuric acid in

the fuel to promote the proton transfer improved the cell performance. However, the overall cell performance slightly dropped when increasing the acid concentration to 0.5 M. The increased acid concentration in the methanol decreased the performance of the conventional fuel cell design with just a CCM and no wall catalyst. The observed results are contrary to the trend reported in the literature⁸⁶. Possible reasons for this difference are the low catalyst loading, low operating temperature, and impurities in our fuel cell.

5.1.2 Micro redox anode fuel cell with catalyzed flow field channel walls

The demonstration of the design of a micro-fuel cell with catalyzed flow field channel walls in an air-breathing micro-redox anode fuel cell (μ RAFC) with the reaction of Fe²⁺/Fe³⁺ redox couple as the anode is one of the important outcomes of this research. It was found that the μ RAFC with a graphite channel (corresponding to catalyzed channel walls) could significantly improve the anode and overall cell performances compared with the fuel cell with inactive channel walls. The graphite channel can increase the number of active sites for the redox reaction and have more efficient mass transfer of redox couple to the electrode surface. Different from the μ DMFC, the catalyzed channel walls do not affect the ionic resistance in the RAFC since no protons are generated on the channel walls.

It was observed when increasing the thickness of the anode layer (carbon paper) on the membrane in the redox fuel cell with a graphite channel, the cell voltage and cathode potential decreased, and the anode performance had no obvious change. It is believed that the increase of carbon paper layer can benefit the redox reaction by providing more

active surface areas, but also inhibit the proton transport into the membrane from the electrolyte. The anode reaction rate is not a limiting factor, but the proton transfer to the cathode is a limiting factor determining the redox fuel cell performance.

The anolyte flow rate and sulfuric acid concentration were both crucial operating parameters affecting the performance. It was found that an increase in the flow rate significantly improved the anode performance, but also decreased the cathode performance. When the flow rate was 2 ml/min and higher, the RAFC with a graphite channel achieved better performance. The reaction rate of the redox couple is very fast, and the mass transfer of redox species is a limiting factor in the RAFC. The increase in flow rate can reduce the anode overpotential by increasing the local concentration of the reactant on the anode surface but also increase the anolyte crossover to the cathode, which increases the cathode overpotential. The combination of these two effects determines the overall fuel cell performance.

In this study, the cell voltage was increased dramatically with an increase of the sulfuric acid concentration from 0.5 M to 2 M for the μ RAFC with a graphite channel, which further shows that the proton transfer to the cathode is a limiting factor determining the performance of redox fuel cell with a graphite channel. The acid solution did not show any negative effect on the anode redox reaction. The design of fuel cells with catalyzed flow field channel walls is very suitable for the redox fuel cell with the features of fast reaction kinetics and no generated protons.

5.1.3 Modeling of micro direct methanol fuel cells with catalyzed flow field channel walls

One of the important outcomes of this work is the development of a simplified 3D model for the fuel cell designs with anode catalyst on the walls. The model helped to understand the behaviors and the effects of different parameters on the performance of the direct methanol fuel cell with anode catalyst on the channel walls. The model can provide significant information for determining the design and operation of DMFCs with catalyzed channel walls. The modeling results demonstrate that the methanol crossover flux for the fuel cell with anode catalyst only on the walls is much higher than that for the other designs with anode catalyst layer on the membrane, resulting in poor cathode and overall cell performances. The modeling results of the cathode performance are better than the experimental results for the fuel cell with catalyst only on the channel walls. This difference in the cathode performance indicates that the model underestimated the negative effect of the methanol crossover on the cathode performance. The model only considered the mixed potential due to the methanol reaction at the cathode, but the poisoning of active sites of the Pt catalyst and the reduced oxygen concentration on the active catalyst sites due to the methanol crossover from the anode may play an important role in affecting the experimental results.

The model shows that the drop of the cathode performance with an increase of the anode catalyst loading on the channel walls (for fuel cells with anode catalyst on both the membrane and channel walls) is due to the increased contribution of the anode on the walls, which leads to an extra ionic potential loss.

The model reveals that the performance of fuel cells with anode catalyst both on the channel walls and the membranes is more affected by the conductivity of the solid-phase ionic conductor when increasing the solution ionic conductivity from 3.7 S/m to 25.1 S/m and/or increasing of the ionic conductivity of the solid ionomer membrane from 0.52 S/m to 3.53 S/m compared to the baseline case. However, the performance of fuel cells with anode catalyst only on the channel walls is more affected by the conductivity of the liquid solution. The conductivity of the acidic solution can increase the contribution proportion of the anode catalyst on the channel walls to the total performance when increasing the solution ionic conductivity from 3.7 S/m to 25.1 S/m in the fuel cell with anode catalyst on both the membrane and channel wall. This ionic conductivity of the solid ionomer membrane did not have any obvious impact on the contribution proportion of the anode wall catalyst.

The model indicates the reduction of the channel dimensions can affect the anode performance by increasing the methanol concentration at the CCM, and the cathode performance by increasing methanol crossover and reducing the ionic resistance for the fuel cells with anode catalyst both on the membrane and the channel walls. For the fuel cells with anode catalyst only on the walls, the reduced channel dimensions did not have an obvious impact on the anode performance but improved the cathode performance by reducing the ionic resistance when the effect of the methanol crossover was neglected. To get better performance for the μ DMFC, the channel dimensions are dependent on the tradeoffs between the mass transfer of methanol, ionic resistance, and methanol crossover.

5.2 Recommendations

- 1 For the experimental design, to better understand the effects of a fuel cell with anode catalyst on the channel walls, a thicker membrane (or methanol crossover resistant membrane) with higher anode and cathode catalyst loadings should be used in the µDMFC to reduce the limitations induced by the methanol crossover and the kinetics of the cathode reaction to the performance. To enhance the fuel cell performance, an optimization of the design in terms of the anode catalyst loading both on the membrane and channel walls is recommended.
- 2 For the experimental setup, the inlet and outlet for the methanol solution were located at the anodic current collector, which was made of a gold-plated stainless steel plate. However, gold peeling occurred over time due to the corrosion of the nickel backing layer beneath the gold layer. It is recommended to build the inlet and outlet directly at the graphite plate to avoid the detrimental effect of the acidic electrolyte on the current collector.
- 3 The effects of the anode catalyst loading on the channel walls and operating conditions for fuel cell design with anode catalyst only on the channel walls were not studied due to its poor performance under the baseline conditions. A thicker membrane (or methanol crossover resistant membrane) with higher cathode catalyst loadings could allow for the examination of these experimental effects for the fuel cells with anode catalyst only on the walls.

- 4 In this work, the anode catalyst was deposited on the channel walls through a spraying method. To obtain a more uniform distribution of the catalyst layer in a micro-channel is very difficult, and it is recommended to examine alternative deposition approaches, such as sputtering coating. This would be particularly important if channel dimensions are reduced further.
- 5 A fuel cell with channel dimensions of 1 mm × 1 mm × 30 mm was investigated in this work. An extension of the experimental work is to test the effects of the channel dimensions and shape on the performance of fuel cells with anode catalyst both on the channel walls and membrane. Micro-channels with much smaller dimensions in width and depth can be built on various substrates, such as a silicon substrate through micro-electro-mechanical systems technology.
- 6 In order to further study the effect of catalyzed channel walls on the performance and mass transfer of methanol, fuel cells with multi-channels can be designed and fabricated in the patterns of parallel and single serpentine. The fuel cells with anode catalyst both on the channel walls and the membrane can be compared with the fuel cell with anode catalyst only on the membrane.
- 7 The 3D DMFC model was developed based on the assumption of single phase conditions regarding the reactions. The generated CO₂ at the anode can affect the transfer of protons generated on the channel walls. The water that crosses over from the anode to the cathode, and that is generated at the cathode can affect the proton

conductivity and oxygen transfer in the fuel cell. It is recommended to develop a more comprehensive DMFC model that considers the effect of two-phase flow in the system.

- 8 The effect of methanol crossover was simplified in the DMFC model. A more comprehensive DMFC model that accounts for the Pt catalyst poisoning and the reduction of the oxygen concentration on the cathode active catalyst sites induced by the methanol crossover is recommended, including these phenomena could result in a better agreement between the experimental and modeling results.
- 9 The DMFC model was applied to simulate the two designs: i) fuel cells with both a wall anode and a membrane anode, and ii) fuel cells with a wall anode only. It is recommended to simulate the effect of anode catalyst loading on the membrane, ionic conductivity of the membrane, and channel geometry on the performance of a conventional fuel cell design with just a CCM and no wall anode. The comparison between the designs can provide a better understanding of the features with respect to the fuel cell designs with catalyzed channel walls.
- 10 The DMFC model was applied to simulate the effect of the anode catalyst loading on the channel walls on the overall cell and individual electrode performances of the fuel cell under the condition of liquid-phase electrolyte conductivity of 3.7 S/m (0.1 M H₂SO₄). To reduce the extra ionic potential loss due to the increased anode catalyst loading on the walls, modeling the effect of the anode catalyst loading on the

channel walls on the fuel cell performance should be done under the condition of a higher electrolyte conductivity, e.g., the conductivity of $0.5 \text{ M H}_2\text{SO}_4$ or $1 \text{ M H}_2\text{SO}_4$.

- 11 To further check the effect of the channel dimensions on the performance of fuel cells with catalyzed channel walls, it is recommended to apply the DMFC model to simulate fuel cells with various channel dimensions and cross-sectional shapes. The performance parameters, e.g., ionic potential loss or fuel mass transfer, as a function of channel dimensions can be obtained.
- 12 Modeling should be done for the redox fuel cell to further understand the phenomena and the limiting factors. The transport mechanisms of ionic species in the electrolyte are migration, diffusion, and convection. In the DMFC model, the proton transfer from the anode to the cathode through diffusion and the convection was neglected, and the proton transfer through electrical migration was described by Ohm's law. A 3D redox fuel cell model would be different from the DMFC model, the reaction of redox species is very fast and not dependent on protons, and therefore the redox-couple reaction can be limited by the mass transfer of ionic species at the electrode surface. The transport of ionic species in terms of diffusion should not be neglected in the RAFCs. Instead of Ohm's law, it is recommended to employ the Nernst-Planck equation, and the electrolyte through migration and diffusion.

Bibliography

- 1. International Energy Agency. World Energy Outlook 2016. (2016).
- 2. Revankar, S. & Majumdar, P. *Fuel Cells: Principles, Design, and Analysis. CRC Press* (2014).
- 3. Andújar, J. M. & Segura, F. Fuel cells: History and updating. A walk along two centuries. *Renew. Sustain. Energy Rev.* **13**, 2309–2322 (2009).
- 4. Grove, W. R. XXIV. On voltaic series and the combination of gases by platinum. *London, Edinburgh, Dublin Philos. Mag. J. Sci.* **14,** 127–130 (1839).
- 5. Hoogers, G. Fuel cell technology handbook. (CRC Press, 2003).
- 6. Mekhilef, S., Saidur, R. & Safari, A. Comparative study of different fuel cell technologies. *Renewable and Sustainable Energy Reviews* **16**, 981–989 (2012).
- U.S. Department of Energy. Comparison of Fuel Cell Technologies. Available at: <u>https://energy.gov/eere/fuelcells/comparison-fuel-cell-technologies</u>.
- Larminie, J. & Dicks, A. *Fuel Cell Systems Explained*. (John Wiley & Sons, Ltd., 2003).
- Diego, A. de., Madariaga, J. M. & Chapela, E. Conductivity of Concentrated Aqueous Solutions of Several Fluorine-Containing Electrolytes in a Wide Range of Concentrations and Temperatures. *J. Chem. Eng. Data* 42, 202–208 (1997).
- 10. Gyenge, E. CHBE 577: Fuel Cells and Electrochemical Engineering Course Notes. (2014).
- Meredith, R. E. & Tobias, C. W. Conductivities in Emulsions. *J. Electrochem. Soc.* **108**, 286–290 (1961).
- 12. Meyers, J. P. & Newman, J. Simulation of the Direct Methanol Fuel Cell. J.

Electrochem. Soc. **149**, A718–A728 (2002).

- 13. Pabby, A. K., Rizvi, S. S. H. & Requena, A. M. S. Handbook of Membrane Separations: Chemical, Pharmaceutical, Food, and Biotechnological Applications, Second Edition. (2015).
- 14. Seo, S. H. & Lee, C. S. A study on the overall efficiency of direct methanol fuel cell by methanol crossover current. *Appl. Energy* **87**, 2597–2604 (2010).
- 15. Reddy, T. Linden's handbook of batteries, Fourth Edition. McGraw-Hill Education (2010).
- Kamarudin, S. K., Daud, W. R. W., Ho, S. L. & Hasran, U. a. Overview on the challenges and developments of micro-direct methanol fuel cells (DMFC). *J. Power Sources* 163, 743–754 (2007).
- Dyer, C. K. Fuel cells for portable applications. *J. Power Sources* **106**, 31–34 (2002).
- Kamarudin, S. K., Achmad, F. & Daud, W. R. W. Overview on the application of direct methanol fuel cell (DMFC) for portable electronic devices. *Int. J. Hydrogen Energy* 34, 6902–6916 (2009).
- 19. Broussely, M. & Archdale, G. Li-ion batteries and portable power source prospects for the next 5–10 years. *J. Power Sources* **136**, 386–394 (2004).
- Sundarrajan, S., Allakhverdiev, S. I. & Ramakrishna, S. Progress and perspectives in micro direct methanol fuel cell. *Int. J. Hydrogen Energy* 37, 8765– 8786 (2012).
- Guo, Z. & Faghri, A. Development of planar air breathing direct methanol fuel cell stacks. *J. Power Sources* 160, 1183–1194 (2006).

- Seong Kee Yoon, Youngseung Na, Y. Joung, J. Park Y. Kim, L. Hu, I. Song, H. C. Direct Methanol Fuel Cell Systems for Portable Applications. in *Fuel Cell Seminar* & *Energy Exposition* (2009).
- Darnell Group Inc. Fuel Cells for Portable Power: Markets, Manufacture and Cost. (2003).
- 24. Kundu, A. *et al.* Micro-fuel cells—Current development and applications. *J. Power Sources* **170**, 67–78 (2007).
- Meyers, J. P. & Maynard, H. L. Design considerations for miniaturized PEM fuel cells. 109, 76–88 (2002).
- 26. Morse, J. D. Micro-fuel cell power sources. *Int. J. Energy Res.* **31**, 576–602 (2007).
- Shimizu, T., Mommaa, T., Mohamedia, M., Osakaa, T. & Sarangapanic, S. Design and fabrication of pumpless small direct methanol fuel cells for portable applications. *J. Power Sources* 137, 277–283 (2004).
- 28. Falcão, D. S., Oliveira, V. B., Rangel, C. M. & Pinto, A. M. F. R. Review on microdirect methanol fuel cells. *Renew. Sustain. Energy Rev.* **34**, 58–70 (2014).
- Nguyen, N.-T. & Chan, S. H. Micromachined polymer electrolyte membrane and direct methanol fuel cells—a review. *J. Micromechanics Microengineering* 16, R1– R12 (2006).
- Motokawa, S., Mohamedi, M., Momma, T., Shoji, S. & Osaka, T. MEMS-based design and fabrication of a new concept micro direct methanol fuel cell (μ-DMFC). *Electrochem. commun.* 6, 562–565 (2004).
- 31. D'Urso, C. *et al.* Development of a planar µDMFC operating at room temperature.

Int. J. Hydrogen Energy 36, 8088–8093 (2011).

- Shen, M., Walter, S., Dovat, L. & Gijs, M. A. . Planar micro-direct methanol fuel cell prototyped by rapid powder blasting. *Microelectron. Eng.* 88, 1884–1886 (2011).
- Sun, M. H. *et al.* Characterization of microfluidic fuel cell based on multiple laminar flow. *Microelectron. Eng.* 84, 1182–1185 (2007).
- 34. Choban, E. R., Markoski, L. J., Wieckowski, A. & Kenis, P. J. A. Microfluidic fuel cell based on laminar flow. *J. Power Sources* **128**, 54–60 (2004).
- 35. Esquivel, J. P. *et al.* Fuel cell-powered microfluidic platform for lab-on-a-chip applications: Integration into an autonomous amperometric sensing device. *Lab Chip* **12**, 4232–4235 (2012).
- Jayashree, R. S. *et al.* Air-Breathing Laminar Flow-Based Microfluidic Fuel Cell. *J. Am. Chem. Soc.* **127**, 16758–16759 (2005).
- Kjeang, E., Djilali, N. & Sinton, D. Microfluidic fuel cells: A review. J. Power Sources 186, 353–369 (2009).
- Ferrigno, R., Stroock, A. D., Clark, T. D., Mayer, M. & Whitesides, G. M. Membraneless vanadium redox fuel cell using laminar flow. *J. Am. Chem. Soc.* **124**, 12930–12931 (2002).
- Choban, E. R., Waszczuk, P. & Kenis, P. J. a. Characterization of Limiting Factors in Laminar Flow-Based Membraneless Microfuel Cells. *Electrochem. Solid-State Lett.* 8, A348–A352 (2005).
- 40. Jayashree, R. S. *et al.* Air-Breathing Laminar Flow-Based Direct Methanol Fuel Cell with Alkaline Electrolyte. *Electrochem. Solid-State Lett.* **9**, A252–A256

(2006).

- 41. Whipple, D. T., Jayashree, R. S., Egas, D., Atanassov, P. & Kenis, P. J. a. Ruthenium cluster-like chalcogenide as a methanol tolerant cathode catalyst in air-breathing laminar flow fuel cells. *Electrochim. Acta* **54**, 4384–4388 (2009).
- Zheng, W., Suominen, A. & Tuominen, A. Discussion on the Challenges of DMFC Catalyst Loading Process for Mass Production. *Energy Procedia* 28, 78–87 (2012).
- 43. Cha, H.-Y. *et al.* Fabrication of all-polymer micro-DMFCs using UV-sensitive photoresist. *Electrochim. Acta* **50**, 795–799 (2004).
- Stanley, K. G. *et al.* A hybrid sequential deposition fabrication technique for micro fuel cells. *J. Micromechanics Microengineering* **15**, 1979–1987 (2005).
- 45. Peng, H.-C. *et al.* Passive cathodic water/air management device for micro-direct methanol fuel cells. *J. Power Sources* **195**, 7349–7358 (2010).
- 46. Aufderheide, B. E. Sputtered Thin Film Coatings; in: A.A. Tracton, Coatings Technology Handbook. (CRC Press/Taylor & Francis, 2006).
- 47. Witham, C. K. Performance of Direct Methanol Fuel Cells with Sputter-Deposited Anode Catalyst Layers. *Electrochem. Solid-State Lett.* **3**, 497–500 (1999).
- 48. Zhang, Y., Lu, J., Shimano, S., Zhou, H. & Maeda, R. Development of MEMSbased direct methanol fuel cell with high power density using nanoimprint technology. *Electrochem. commun.* **9**, 1365–1368 (2007).
- 49. Kelley, S. C., Deluga, G. A. & Smyrl, W. H. A miniature methanol/air polymer electrolyte fuel cell. *Electrochem. SOLID STATE Lett.* **3**, 407–409 (2000).
- 50. Yeom, J. et al. Microfabrication and characterization of a silicon-based millimeter

scale, PEM fuel cell operating with hydrogen, methanol, or formic acid. *Sensors Actuators B Chem.* **107**, 882–891 (2005).

- Tominaka, S., Ohta, S., Obata, H., Momma, T. & Osaka, T. On-chip fuel cell: micro direct methanol fuel cell of an air-breathing, membraneless, and monolithic design. *J. Am. Chem. Soc.* **130**, 10456–10457 (2008).
- 52. Bae, B. *et al.* Performance evaluation of passive DMFC single cells. *J. Power Sources* **158**, 1256–1261 (2006).
- 53. Havránek, A., Klafki, K. & Wippermann, K. The influence of the catalyst loading and the ionomer content on the performance of DMFC anodes. in *2nd International Conference on Advanced Batteries and Accumulators* 32–1 (2001).
- Liu, X. *et al.* Development and characterization of a novel air-breathing micro direct methanol fuel cell stack for portable applications. *J. Micromech. Microeng.* 20, 104008–104018 (2010).
- 55. Zhang, Q. *et al.* Design, optimization and microfabrication of a micro-direct methanol fuel cell with microblocks in anode structure. *Sensors Actuators, A Phys.* **154**, 247–254 (2009).
- Zhang, B. *et al.* Development and performance analysis of a metallic micro-direct methanol fuel cell for high-performance applications. *J. Power Sources* 195, 7338–7348 (2010).
- 57. Kulikovsky, A. A. The voltage-current curve of a direct methanol fuel cell: 'Exact' and fitting equations. *Electrochem. commun.* **4**, 939–946 (2002).
- 58. Scott, K., Taama, W., Haslar, D. R. A. & Britain, G. Performance of a direct methanol fuel cell. *J. Appl. Electrochem.* **28**, 289–297 (1998).

- 59. Wainright, J. S., Savinell, R. F., Liu, C. C. & Litt, M. Microfabricated fuel cells. *Electrochim. Acta* **48**, 2869–2877 (2003).
- Li, P. W., Zhang, T., Wang, Q. M., Schaefer, L. & Chyu, M. K. The performance of PEM fuel cells fed with oxygen through the free-convection mode. *J. Power Sources* 114, 63–69 (2003).
- 61. Hottinen, T., Mikkola, M. & Lund, P. Evaluation of planar free-breathing polymer electrolyte membrane fuel cell design. *J. Power Sources* **129**, 68–72 (2004).
- Litster, S., Pharoah, J. G., McLean, G. & Djilali, N. Computational analysis of heat and mass transfer in a micro-structured PEMFC cathode. *J. Power Sources* 156, 334–344 (2006).
- R. Hahn, S. Wagner, A. Schmitz, H. R. Development of a planar micro fuel cell with thin film and micro patterning technologies. *J. Power Sources* **131**, 73–78 (2004).
- 64. Ponce de León, C., Frías-Ferrer, A., González-García, J., Szánto, D. A. & Walsh,
 F. C. Redox flow cells for energy conversion. *J. Power Sources* 160, 716–732 (2006).
- Joerissen, L., Garche, J., Fabjan, C. & Tomazic, G. Possible use of vanadium redox-flow batteries for energy storage in small grids and stand-alone photovoltaic systems. *J. Power Sources* **127**, 98–104 (2004).
- Alotto, P., Guarnieri, M., Moro, F. & Stella, A. Large scale energy storage with redox flow batteries. COMPEL Int. J. Comput. Math. Electr. Electron. Eng. 32, 1459–1470 (2013).
- 67. Alotto, P., Guarnieri, M. & Moro, F. Redox flow batteries for the storage of

renewable energy: A review. Renew. Sustain. Energy Rev. 29, 325–335 (2014).

- Parasuraman, A., Lim, T. M., Menictas, C. & Skyllas-Kazacos, M. Review of material research and development for vanadium redox flow battery applications. *Electrochim. Acta* **101**, 27–40 (2013).
- Chakrabarti, M. H. *et al.* Application of carbon materials in redox flow batteries. *J. Power Sources* 253, 150–166 (2014).
- Kjeang, E., McKechnie, J., Sinton, D. & Djilali, N. Planar and three-dimensional microfluidic fuel cell architectures based on graphite rod electrodes. *J. Power Sources* 168, 379–390 (2007).
- 71. Weber, A. Z. *et al.* Redox flow batteries: A review. *J. Appl. Electrochem.* **41**, 1137–1164 (2011).
- 72. Ilicic, A. B., Wilkinson, D. P., Fatih, K. & Girard, F. High Fuel Concentration Direct-Liquid Fuel Cell with a Redox Couple Cathode. *J. Electrochem. Soc.* **155**, B1322– B1327 (2008).
- 73. Giner, J., Swette, L. & Cahill, K. Screening of redox couples and electrode materials. NASA CR-134705 (1976).
- 74. Fatih, K., Wilkinson, D. P., Moraw, F., Ilicic, A. & Girard, F. Advancements in the Direct Hydrogen Redox Fuel Cell. *Electrochem. Solid-State Lett.* **11**, B11 (2008).
- Dara, M. S., Lam, A., Fatih, K. & Wilkinson, D. P. Low Cost Hydrogen Fuel Cell. ECS Trans. 45, 109–119 (2013).
- 76. Ilicic, A. B., Dara, M. S., Wilkinson, D. P. & Fatih, K. Improved performance of the direct methanol redox fuel cell. *J. Appl. Electrochem.* **40**, 2125–2133 (2010).
- 77. Kaneko, H., Negishi, A., Nozaki, K., Sato, K. & Nakajima, M. Redox Battery. US

Patent 5318865 (1992).

- Menictas, C. & Skyllas-Kazacos, M. Performance of vanadium-oxygen redox fuel cell. *J. Appl. Electrochem.* 41, 1223–1232 (2011).
- Austing, J. grosse, Kirchner, C. N., Hammer, E.-M., Komsiyska, L. & Wittstock, G. Study of an unitised bidirectional vanadium/air redox flow battery comprising a two-layered cathode. *J. Power Sources* 273, 1163–1170 (2015).
- Noack, J., Cremers, C., Bayer, D., Tübke, J. & Pinkwart, K. Development and characterization of a 280 cm2 vanadium/oxygen fuel cell. *J. Power Sources* 253, 397–403 (2014).
- 81. Li, J., Moore, C. & Kohl, P. A. Investigation of acidic methanol solution as a fuel for microchannel fuel cells. *J. Power Sources* **138**, 211–215 (2004).
- 82. Liu, L. *et al.* Carbon supported and unsupported Pt–Ru anodes for liquid feed direct methanol fuel cells. *Electrochim. Acta* **43**, 3657–3663 (1998).
- Liu, F. *et al.* Development of novel self-humidifying composite membranes for fuel cells. *J. Power Sources* 124, 81–89 (2003).
- Ciureanu, M. & Roberge, R. Electrochemical impedance study of PEM fuel cells.
 Experimental diagnostics and modeling of air cathodes. *J. Phys. Chem. B* 105, 3531–3539 (2001).
- 85. Zhang, Y. *et al.* A self-breathing metallic micro-direct methanol fuel cell with the improved cathode current collector. *Int. J. Hydrogen Energy* **36**, 857–868 (2011).
- Kumar, P., Dutta, K. & Kundu, P. P. Enhanced performance of direct methanol fuel cells : a study on the combined effect of various supporting electrolytes , flow channel designs and operating temperatures. 38, 41–50 (2014).
- Prabhuram, J. & Manoharan, R. Investigation of methanol oxidation on unsupported platinum electrodes in strong alkali and strong acid. *J. Power Sources* 74, 54–61 (1998).
- Covington, A. K., Bates, R. G. & Durst, R. A. Definition of pH scales, standard reference values, measurement of pH and related terminology. *Pure Appl. Chem.* 57, 531–542 (1985).
- Wang, W. *et al.* Recent progress in redox flow battery research and development.
 Adv. Funct. Mater. 23, 970–986 (2013).
- 90. Pattabiraman, R., Venkatesan, V. K. & Udupa, H. V. K. Applications of redox systems in fuel cells. *J. Sci. Ind. Res.* **40**, 432–447 (1981).
- 91. Kummer, J. T. & Oei, D. G. A chemically regenerative redox fuel cell. II. *J. Appl. Electrochem.* **15**, 619–629 (1985).
- Adams, G. B. & Hollandsworth, R. P. Electrochemical Oxidation of Ferrous Iron in Very Dilute Solutions. **122**, 1043–1048 (1972).
- 93. Mazuelos, A., Carranza, F., Palencia, I. & Romero, R. High efficiency reactor for the biooxidation of ferrous iron. *Hydrometallurgy* **58**, 269–275 (2000).
- 94. Fatiha, K., Wilkinsona, D. P., Morawa, F. & Francois, G. Evaluation of the Fe3+/Fe2+ Redox Fuel Cell Cathode Couple. in *207th ECS Meeting* 1579 (2005).
- Ilicic, A. B., Wilkinson, D. P. & Fatih, K. Advancing Direct Liquid Redox Fuel Cells: Mixed-Reactant and In Situ Regeneration Opportunities. *J. Electrochem. Soc.* 157, B529–B535 (2010).
- 96. Pradhan, B. K. & Sandle, N. K. Effect of different oxidizing agent treatments on the surface properties of activated carbons. *Carbon N. Y.* **37**, 1323–1332 (1999).

- 97. Aziznia, A., Oloman, C. W. & Gyenge, E. L. Platinum- and membrane-free swissroll mixed-reactant alkaline fuel cell. *ChemSusChem* **6**, 847–855 (2013).
- Carmo, M., Linardi, M. & Poco, J. G. R. Characterization of nitric acid functionalized carbon black and its evaluation as electrocatalyst support for direct methanol fuel cell applications. *Appl. Catal. A Gen.* 355, 132–138 (2009).
- 99. Wang, Z. H. & Wang, C. Y. Mathematical Modeling of Liquid-Feed Direct Methanol Fuel Cells. *J. Electrochem. Soc.* **150**, A508–A519 (2003).
- Scott, K., Argyropoulos, P. & Sundmacher, K. A model for the liquid feed direct methanol fuel cell. *J. Electroanal. Chem.* 477, 97–110 (1999).
- 101. Colpan, C. O., Fung, A. & Hamdullahpur, F. 2D modeling of a flowing-electrolyte direct methanol fuel cell. *J. Power Sources* **209**, 301–311 (2012).
- 102. Kjeang, E. *et al.* A parametric study of methanol crossover in a flowing electrolytedirect methanol fuel cell. *J. Power Sources* **153**, 89–99 (2006).
- 103. Ye, D., Zhu, X., Liao, Q., Li, J. & Fu, Q. Two-dimensional two-phase mass transport model for methanol and water crossover in air-breathing direct methanol fuel cells. *J. Power Sources* **192**, 502–514 (2009).
- Oliveira, V. B., Falcão, D. S., Rangel, C. M. & Pinto, A. M. F. R. Heat and mass transfer effects in a direct methanol fuel cell: A 1D model. *Int. J. Hydrogen Energy* 33, 3818–3828 (2008).
- Rosenthal, N. S., Vilekar, S. A. & Datta, R. A comprehensive yet comprehensible analytical model for the direct methanol fuel cell. *J. Power Sources* 206, 129–143 (2012).
- 106. He, Y., Li, X., Miao, Z. & Liu, Y. Two-phase modeling of mass transfer

characteristics of a direct methanol fuel cell. *Appl. Therm. Eng.* **29**, 1998–2008 (2009).

- 107. García, B. L., Sethuraman, V. a., Weidner, J. W., White, R. E. & Dougal, R. Mathematical Model of a Direct Methanol Fuel Cell. *J. Fuel Cell Sci. Technol.* 1, 43–48 (2004).
- Eccarius, S., Garcia, B. L., Hebling, C. & Weidner, J. W. Experimental validation of a methanol crossover model in DMFC applications. *J. Power Sources* 179, 723–733 (2008).
- 109. Gogel, V. *et al.* Performance and methanol permeation of direct methanol fuel cells : dependence on operating conditions and on electrode structure. **127**, 172–180 (2004).
- 110. Kumar, A., Pramanik, S. & Mishra, M. COMSOL Multiphysics® Modeling in Darcian and Non-Darcian Porous Media. in *COMSOL conference* (2016).
- Ubong, E. U., Shi, Z. & Wang, X. Three-dimensional modeling and experimental study of a high temperature PBI-based PEM fuel cell. *J. Electrochem. Soc.* 156, B1276–B1282 (2009).
- 112. Zhang, B., Ye, D., Sui, P.-C., Djilali, N. & Zhu, X. Computational modeling of airbreathing microfluidic fuel cells with flow-over and flow-through anodes. *J. Power Sources* **259**, 15–24 (2014).
- 113. Saarinen, V., Himanen, O., Kallio, T., Sundholm, G. & Kontturi, K. A 3D model for the free-breathing direct methanol fuel cell: Methanol crossover aspects and validations with current distribution measurements. *J. Power Sources* **172**, 805– 815 (2007).

- 114. Hussaini, I. S. & Wang, C. Y. Measurement of relative permeability of fuel cell diffusion media. *J. Power Sources* **195**, 3830–3840 (2010).
- 115. Ge, J. & Liu, H. A three-dimensional mathematical model for liquid-fed direct methanol fuel cells. *J. Power Sources* **160**, 413–421 (2006).
- 116. Yang, W. W. & Zhao, T. S. A two-dimensional , two-phase mass transport model for liquid-feed DMFCs. **52**, 6125–6140 (2007).
- 117. Yang, W. W. & Zhao, T. S. Two-phase , mass-transport model for direct methanol fuel cells with effect of non-equilibrium evaporation and condensation. **174**, 136– 147 (2007).
- 118. Chen, R. & Zhao, T. S. Mathematical modeling of a passive-feed DMFC with heat transfer effect. **152**, 122–130 (2005).
- 119. Xu, C., Zhao, T. S. & Yang, W. W. Modeling of water transport through the membrane electrode assembly for direct methanol fuel cells. **178**, 291–308 (2008).
- 120. Bahrami, H. & Faghri, A. Review and advances of direct methanol fuel cells: Part II: Modeling and numerical simulation. *J. Power Sources* 230, 303–320 (2013).
- Tamaki, T., Yamauchi, A., Ito, T., Ohashi, H. & Yamaguchi, T. The Effect of Methanol Crossover on the Cathode Overpotential of DMFCs. *Fuel cells* **11**, 394– 403 (2011).
- 122. Kulikovsky, A. A. A model for mixed potential in direct methanol fuel cell cathode. *Electrochim. Acta* **62**, 185–191 (2012).
- 123. Jeffrey A. Kolde, B. B. & Gore, W. L. Advanced Composite Polymer Electrolyte Fuel Cell Membranes. in *Proceedings of the First International Symposium on*

Proton Conducting Membrane Fuel Cells 95–23, 193–201 (1995).

Appendices



Appendix A: Dimensioned drawings of the fuel cell components

Figure A.1 Dimensioned drawing of the stainless steel anode current collector plate.



Figure A.2 Dimensioned drawing of the stainless steel cathode current collector plate.



Figure A.3 Dimensioned drawing of the graphite channel plate.



Figure A.4 Dimensioned drawing of the fuel cell holder on the top.



Figure A.5 Dimensioned drawing of the fuel cell holder on the bottom.

Appendix B: SEM photo of the catalyst coated membrane



Figure B.1 SEM photo of the cross-sectional view of the catalyst coated membrane: (A) Pt/C anode catalyst layer, 0.44 mg_{Pt}/cm^2 ; (B) membrane; (C) Pt/C cathode catalyst layer, 0.04 mg_{Pt}/cm^2 .

Appendix C: Electrochemical impedance spectra



C.1 Impedance spectra of the DMFC

Figure C.1 a) Nyquist plots at the OCV for μ DMFCs with different anode catalyst distributions at ambient temperature and pressure and 1 M methanol/0.1 M sulfuric acid at a flow rate of 0.1 ml/min; b) an expansion of the high frequency region of the Nyquist plots.



Figure C.2 a) Nyquist plots at the OCV for μ DMFCs with anode catalyst deposited both on the membrane and channel walls for different loading of Pt on the channel walls at ambient temperature and pressure and 1 M methanol mixed with 0.1 M sulfuric acid at a flow rate of 0.1 ml/min; b) an expansion of the high frequency region of the Nyquist plots.



Figure C.3 a) Nyquist plots at the OCV for μ DMFCs with anode catalyst deposited both on the membrane and channel walls under different sulfuric acid concentrations at ambient temperature and pressure and 1 M methanol mixed with 0.1 M sulfuric acid at a flow rate of 0.1 ml/min; b) an expansion of the high frequency region of the Nyquist plots.



Figure C.4 a) Nyquist plots at the OCV for µDMFCs with anode catalyst deposited on the membrane only under different sulfuric acid concentrations at ambient temperature and pressure and 1 M methanol mixed with 0.1 M sulfuric acid at a flow rate of 0.1 ml/min; b) an expansion of the high frequency region of the Nyquist plots.



Figure C.5 a) Nyquist plots at the OCV for μ DMFCs with anode catalyst deposited both on the membrane and channel walls under different air supply modes at ambient temperature and pressure and 1 M methanol mixed with 0.1 M sulfuric acid at a flow rate of 0.1 ml/min; b) an expansion of the high frequency region of the Nyquist plots.

C.2 Impedance spectra of the µRAFC



Figure C.6 a) Nyquist plots at the OCV for μ RAFCs with different channel material at ambient temperature and pressure and 1 M FeSO₄/1 M H₂SO₄ at a flow rate of 0.1 ml/min.; b) an expansion of the high frequency region of the Nyquist plots; b) an expansion of the high frequency region of the Nyquist plots.



Figure C.7 a) Nyquist plots at the OCV for μ RAFCs with a graphite channel and different layers of carbon paper at ambient temperature and pressure and 1 M FeSO₄/1 M H₂SO₄ at a flow rate of 0.1 ml/min; b) an expansion of the high frequency region of the Nyquist plots.



Figure C.8 a) Nyquist plots at the OCV for μ RAFCs with a graphite channel for different sulfuric acid concentrations at ambient temperature and pressure and 1 M FeSO₄/H2SO₄ at a flow rate of 0.1 ml/min; b) an expansion of the high frequency region of the Nyquist plots.

Appendix D: The membrane conductivity measurement

The membrane conductivity was evaluated using a measuring cell as shown in Figure D.1 (a). In the cell, one piece of membrane specimen with a diameter of 18 mm was pressed between two pieces of Toray carbon paper TGP-H-030 with a diameter of 16 mm and two gold plates as shown in Figure D.1 (c). The measuring cell was placed in 0.1 M sulfuric acid solution during the EIS measurement. The impedance spectra were collected by a Biologic VMP3 at open circuit voltage by applying an AC amplitude of 10 mV in a frequency range from 0.1 Hz to1000 kHz. The total resistance R_t between the two gold plates was determined by the intercept at high frequency on the real axis in the Nyquist plots of the EIS measurements, as shown in Figure D.2.



Figure D.1 a) Conductivity measuring cell; b) gold coated plate; c) schematic cross-sectional view of the arrangements in the measuring cell.

The conductivity σ_m of the membrane was calculated by the following equation:

$$\sigma_m = \frac{t_m}{R_m A} \tag{D.1}$$

where *L* is the membrane thickness (0.017 mm); *A* is the electrode area (2 cm²); and R_m is the membrane resistance (Ω). R_m was estimated by the difference of R_t (0.180± 0.001 Ω) and $R_{electron}$ (0.0180±0.0001 Ω), where $R_{electron}$ is the electrical resistance between the two gold plates without a membrane. The conductivity σ_m is 0.52±0.01 S/m.



Figure D.2 Nyquist plots at the OCV for the measuring cell with a membrane compressed by carbon papers and gold coated plates.